”Bulk and trace elements" in saline water produced from the Danish North Sea: The chemical analysis and the trends in the retrieved data

Nitsche Gottfredsen, Sofie; Schovsbo, Niels; Feilberg, Karen Louise

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BOOK OF ABSTRACTS

European Winter Conference on Plasma Spectrochemistry

PAU

Feb. 3 - 8
2019

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PAU BÉARN PYRÉNÉES Communauté d'Agglomération
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Programme

Elemental Scientific
welcomes you to EWCPS 2019

prep*FAST* IC

NWR193

What's New

Monday, February 4th Poster Session

- **MP-29 Improving laboratory efficiency with a combined prep*FAST* and chromatography method for chromium speciation** - C Derrick Quarles Jr, Michael Szoltysik, Patrick Sullivan, Maurice Reijnen

- **MP-30 Inline sample preparation system for micro volume clinical samples** - C Derrick Quarles Jr, Stephen Sudyka, Austin Schultz, M. Paul Field, Daniel Wiederin

- **MP-31 Automated laser ablation sampling for food safety** - C Derrick Quarles Jr, Todor Todorov, Ciaran O'Connor, Rob Hutchinson, Katherine McLachlin

- **MP-32 Advantages of inline dilution for LC-ICP MS based applications involving arsenic speciation** - C Derrick Quarles Jr, Patrick Sullivan, M. Paul Field, Daniel Wiederin

- **MP-63 High volume in-line syringe dilution system for ICPOES and ICP MS** - Andrew Toms, Austin Schultz, Daniel Wiederin

- **MP-64 Automated preconcentration and matrix removal for ultratrace determination of radium in environmental waters** - Nathan Saetveit, Aurelien Viscardi

Social

Monday, February 4th at 20:00 (8pm)

Join us for cocktails and hors d'oeuvres
Le Poulet à 3 Pattes
26 Blvd. des Pyrénées

Lunch

Wednesday, February 6th 12:25-14:00

Lunch Seminar
Monzepat Room
Conference Center

Elemental Scientific

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Dear Plasma Spectrochemists,
Dear Colleagues,

It is my great honor and pleasure to welcome you to the 2019 European Winter Conference on Plasma Spectrochemistry held from February 3 to 8, 2019, in Pau, a historical royal city set at the foot of the Pyrenees mountains. The current EWCPS-2019 is the 18th event in this well-established series of successful meetings organized by European research groups alternating yearly with the US conferences organized by Professor Ramon Barnes .

Once again, the Winter Plasma Spectrochemistry Conference brings together the major figures in the field and attracts over 500 participants to present their work and exchange on all the topics concerning analytical plasma spectrochemistry and related mass and emission spectrometric techniques, including fundamentals and instrumentation, sample introduction techniques, glow discharge, laser ablation, isotopic analysis, speciation and metallomics, quality control and industrial applications.

We are proposing outstanding plenary, keynote and heritage lectures as well as more than 70 contributed talks and 300 posters. The program is complemented by a number of special sessions, workshops and technical short courses taught by renowned experts. The EWCPS-2019 is hosting the exhibition where companies introduce and present their latest products in a warm and convivial atmosphere and setting.

I am particularly pleased to welcome Prof. José Ignacio Garcia Alonso and Dr. Magdalena Matczuk, the awardees of two prizes (2019 European Award for Plasma Spectrochemistry and the Rising Star Award for Plasma Spectrochemistry, respectively) sponsored by Agilent Technologies and promoting analytical plasma spectrochemical developments and applications in Europe. I am also happy to extend my congratulations to the two other laureates of the awards presented at the EWCPS-2019 - Dr. Dominic Hare, the Emerging Leader in Atomic Spectroscopy Awardee and Dr. Marcia Foster Mesko, the JAAS Emerging Investigator Lecturer.

I warmly and sincerely extend my welcome to the young scientists seeking to share and expand their experiences in plasma spectrochemistry and especially those who have won one of 12 PhD students grants covering their participation at the conference in exchange for a high-impact lecture. A Young Scientists Career event provides opportunities of networking and discussing with world leading scientists and companies managers the best ways to pursue a career in industry or academia.

I wish you all a productive and successful conference, an unforgettable cultural and culinary experience and lots of fun during the social events.

Ryszard Lobinski

Chair of the 2019 European Winter Conference on Plasma Spectrochemistry

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Joanna Szpunar
CNRS, Pau, France
Programme Chair

Hugues Paucot
UT2A Training & Consulting,
Pau, France
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- Bastien Duval
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- Alexandr Ivaneev
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General information

CONFERENCE VENUE

The conference will be held in the Palais Beaumont, the historic conference centre with a panoramic view of the Pyrenees, just a few minutes' walk from the city center. We kindly remind you that the access to the Palais Beaumont is allowed only upon presenting the conference badge.

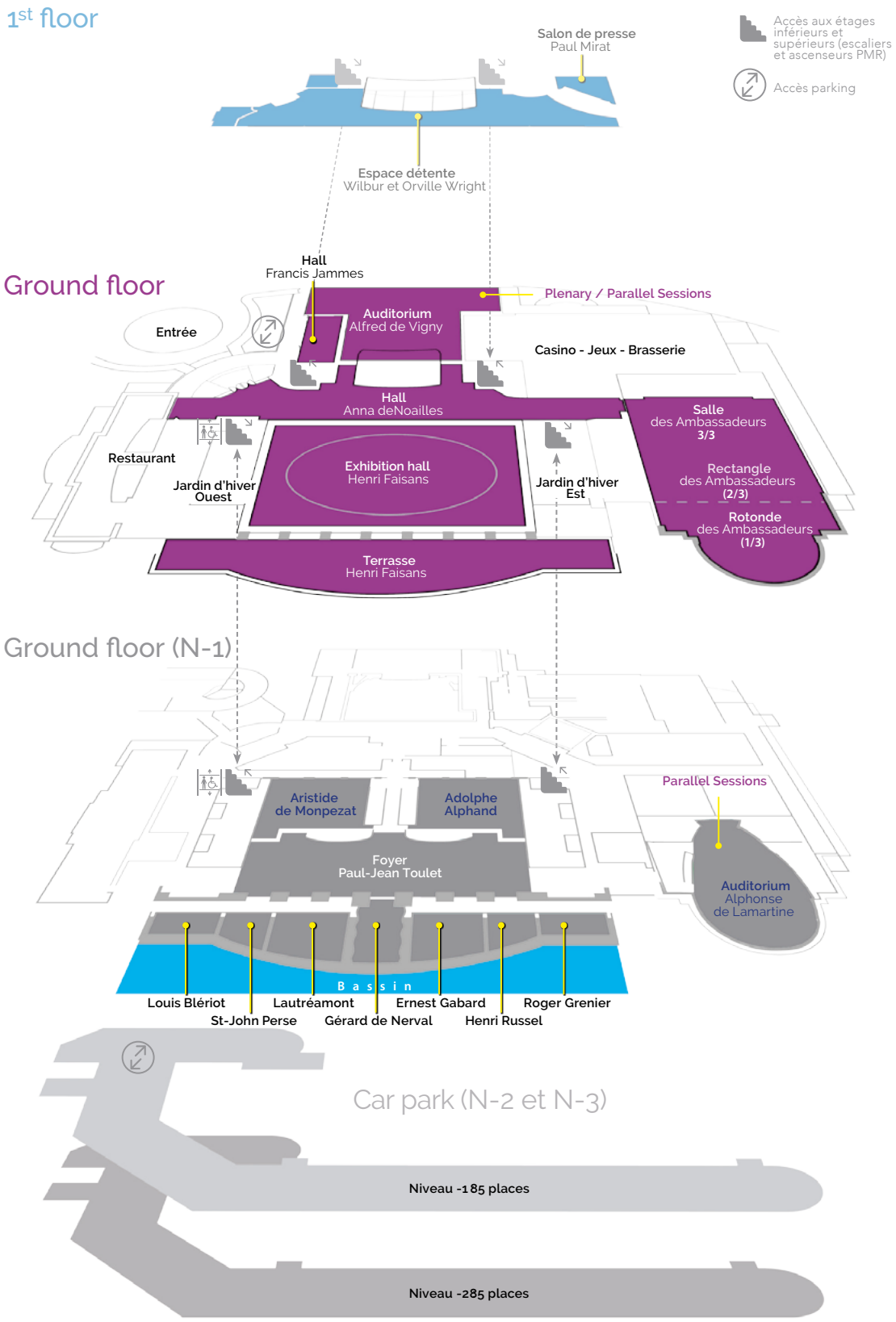
CONFERENCE SECRETARIAT

ADERA Congrès
162 avenue Albert Schweitzer
33608 Pessac Cedex, France
ewcps2019@adera.fr

LE PALAIS BEAUMONT

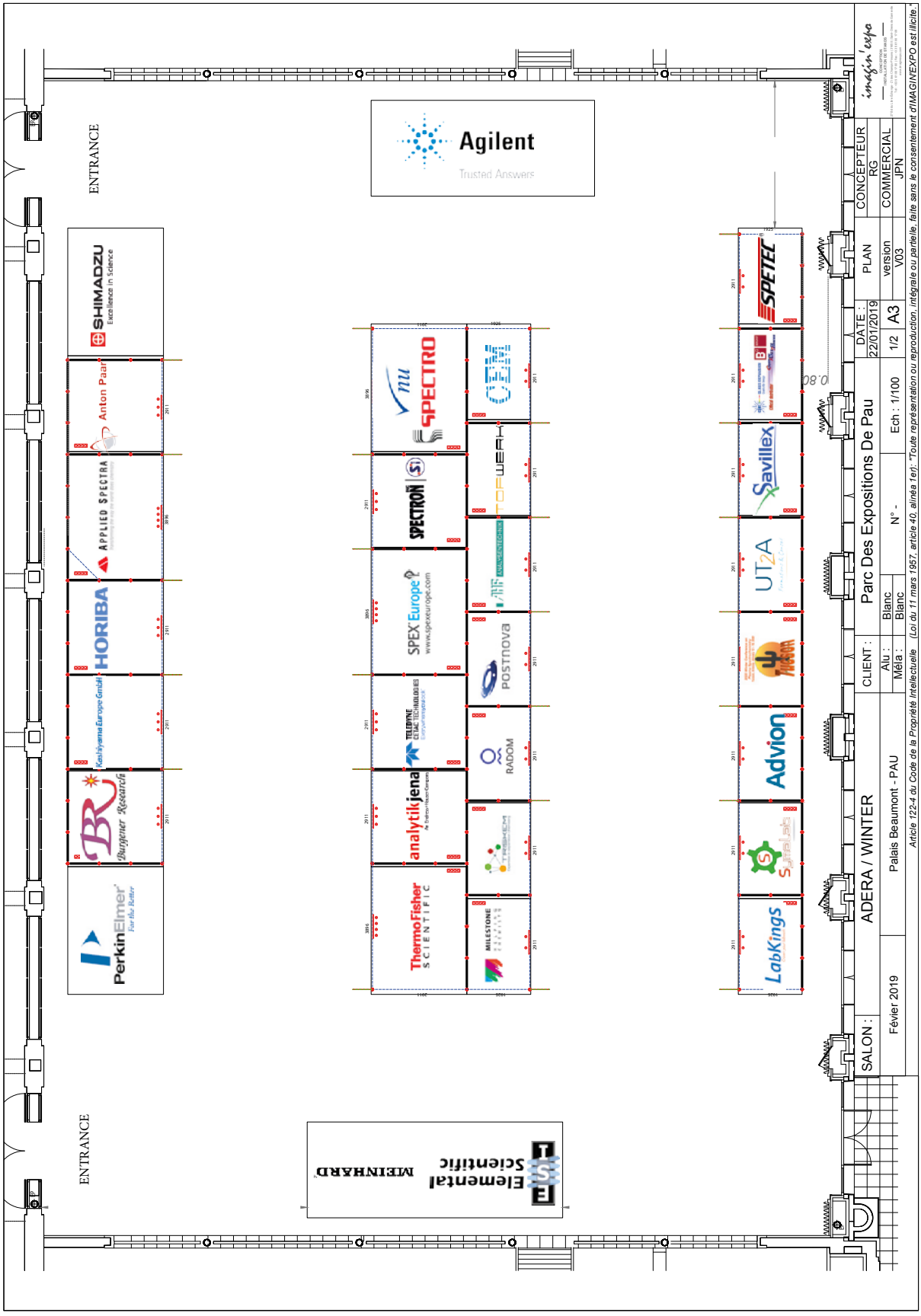
Allée Alfred de Musset
64000 Pau, France
Tel: +33 (0)8 05 02 20 15

FLOOR MAP


1st floor
Salon de presse
Paul Mirat
Accès aux étages inférieurs et supérieurs (escaliers et ascenseurs PMR)
Accès parking
Espace détente
Wilbur et Orville Wright
Ground floor
Hall
Francis Jammes
Plenary / Parallel Sessions
Auditorium
Alfred de Vigny
Entrée
Casino - Jeux - Brasserie
Hall
Anna deNoailles
Salle
des Ambassadeurs
3/3
Restaurant
Exhibition hall
Henri Faisans
Jardin d'hiver
Ouest
Jardin d'hiver
Est
Rectangle
des Ambassadeurs
(2/3)
Rotonde
des Ambassadeurs
(1/3)
Terrasse
Henri Faisans
Ground floor (N-1)
Parallel Sessions
Aristide
de Monpezat
Adolphe
Alphand
Foyer
Paul-Jean Toulet
Auditorium
Alphonse
de Lamartine
Bassin
Louis Blériot
St-John Perse
Lautréamont
Gérard de Nerval
Ernest Gabard
Henri Russel
Roger Grenier
Car park (N-2 et N-3)
Niveau -1 85 places
Niveau -2 85 places

EXHIBITION

The exhibition of analytical instruments, laboratory equipment and scientific literature will take place in the *Henri Faisans* hall. It will open on Sunday, February 3rd, 2019 at 19:00 and close on Friday, February 8th, 2019 at 11:00. Booths can be visited during coffee breaks, lunch breaks and poster sessions as well as during the lectures.



Lectures and oral presentations

All presentations should be displayed using the conference multimedia system. They should be prepared in .pptx format. The presenters are requested to upload their presentations at least 1 hour before the session during which the presentation will be given.

Posters

The maximum dimension of the posters is A0 (841 x 1189 mm). Poster sessions will take place in the *Salle Ambassadeurs*. The organizers will provide all the materials necessary to fix the posters onto the boards.

Notice : Monday and Tuesday posters should be displayed from Monday 8:30 till Tuesday 18:00; Wednesday and Thursday posters should be displayed from Wednesday 8:30 till Thursday 13:00. The presence of at least one of the authors in front of the poster is requested on the day of the corresponding session.

Short courses

A number of short courses given related to techniques and methods of plasma spectrochemistry will be given by the specialists in the field; the courses will take place on Sunday morning and early afternoon.

Vendors' Lunch seminars and workshops

A number of lunch seminars and workshops presenting the latest development in analytical instrumentation will be proposed by the EWCPS-2019 partners. They will be organized by :

• **Anton Paar** - Lunch seminar
(*room Monpezat*)
Monday, February 4th (12:25-14:00)

• **Shimadzu** – Lunch seminar
(*room Alphand*)
Monday, February 4th (12:25-14:00)

• **Agilent** :

– Workshop
(*Auditorium Alphonse de Lamartine*)
Monday, February 4th (17:30-19:00)

–Lunch seminar
(*room Alphand*)
Tuesday, February 5th (12:25-14:00)

• **Elemental Meinhard** - Lunch seminar
(*room Monpezat*)
Wednesday, February 6th (12:25-14:00)

• **Thermo Fisher Scientific** - Lunch seminar
(*room Alphand*)
Wednesday, February 6th (12:25-14:00)

• **Ametek Spectro** – Users' meeting
(*room Lautréamont*)
Wednesday, February 6th (17:30-19:00)

• **PerkinElmer** - Lunch seminar
(room Monpezat)
Thursday, February 7th (12:25-14:00)

• **Horiba** - Users' meeting
(*room Alphand*)
Wednesday, February 6th (17:30 – 19:00)

Glow Discharge Workshop

Workshop on analytical glow discharge will be held on Tuesday, 5th February, 11.00 -12.25 (room Gabard). The aim of this workshop is the exchange of information and experience between experts in the field of analytical glow discharge and newcomers.

Young Scientist Career Event

Young Scientist Career Event is scheduled on Thursday, February 7th at 17:30 (Monpezat room) and aimed to provide information about possible career options in science and research as well as job options in industry for young scientists at the end of their doctoral studies as well as for post-doc researchers that are looking for new challenges. The participating senior researchers from academia, public research organizations and private companies will give short presentations highlighting their expectations and criteria applied when hiring new staff. Then they will answer questions of the young audience and will be available for individual discussions with young researchers.

Social events

Offered to all the registered participants and accompanying persons :

• **Get-together party** will take place at the very beginning of the conference just after the opening session (evening February 3rd, 2019). The attendees will have an opportunity to meet old and make new friends and get the first taste of the South Western French cuisine accompanied by local wines.

• **Lunches** and **coffee** will be served in the exhibition area

• **Guided visit of the Pau Castle** will take place on Friday, February 8th, 2019 afternoon; on request, additional visits on Tuesday, Wednesday (at 10:30 and 15:30) and Thursday (at 14:30) can be available. Several groups with English, French and Spanish speaking guides will be organized.

Optional (additional participation fee required) :

• The European Winter Conference on Plasma Spectrometry **Hot Plasma Party** (sponsored by Thermo Fisher Scientific) will be held in the traditional wine producing château "*Domain Cinquau*" surrounded by superb views of the Béarn countryside. You will be able to enjoy the rich atmosphere of this special place tasting not only some of the finest local wines, but also the best cuisine the Béarn region has to offer. The party will be animated by a band orchestra playing popular traditional and contemporary tunes.
The buses will leave from the conference center at 18:45.

• **Gala Dinner** will be held on Thursday, February 7th, 2019 evening will be a perfect opportunity to unwind, enjoy a meal with your new and old colleagues and be entertained. A five-course dinner with wine will be served in the exquisite the *Salle des Ambassadeurs* of the Palais Beaumont and accompanied by a music performance. At the end of the evening, you will have an opportunity to appreciate the Armagnac tasting.

Vendors' Social Evening Events
Several social events will be organized on Monday, February 4th and Wednesday, February 6th evenings by conference partners who will contact the participants directly with invitation and programme details.

SUNDAY

08:15 **Registration**

09:00 **Short Courses**
SC-1 Metrology for spectrochemical measurements (room Nerval)
SC-2 Nanomaterials (room Gabar)
SC-3 Isotope and isotope diluton ICP MS (room Lautreamont)

12:00

13:30 **Short Courses**
SC-4 ICP MS/MS fundamentals (room Nerval)
SC-5 Speciaton analysis (room Grenier)
SC-6 Laser Ablaton ICP MS (room Gabar)
SC-7 Single Particle and Single Cell Analysis (room Lautreamont)

16:30

17:00 **OPENING CEREMONY**
Auditorium Alfred de Vigny

19:15 **GET-TOGETHER PARTY**
Room Henri Faisans

MONDAY

08:30 **PLM-1:** A. Bengtson

09:15 **KM-1:** V. Hofmann

09:40 **KM-2:** J. Pisonero

10:05 **Coffee Break**

10:45	**KM-3:** T. Iwai	**KM-4:** Z. Weiss
11:10	**OM-01:** A. Hrdlička	**OM-02:** J. Fandiño
11:25	**OM-03:** E. B.-Fernandez	**OM-04:** B. Stankov
11:40	**OM-05:** M. Wong	**OM-06:** A. Ganeev
11:55	**OM-07:** I. Gornushkin	**OM-08:** L. Lobo
12:10	**OM-09:** A. Pastor	**OM-10:** V. Brückel

12:25 **LUNCH BUFFET -** Exhibition Hall
LUNCH SEMINARS - Rooms Alphand/Monpezat

14:00 **POSTER SESSION**

15:10	**KM-5:** H. Goenanga	**KM-6:** J. Ruiz
15:35	**OM-11:** F. Laborda	**OM-12:** A. Raab
15:50	**OM-13:** K. Inagaki	**OM-14:** T. Garcia-Barrera
16:05	**OM-15 :** D. Mozhayeva	**OM-16:** C. Swart
16:20	**OM-17:** K. Chun	**OM-18:** L. Ouerdane

16:35
16:40 **Heritage Lecture:** A. Montaser
Auditorium Alfred de Vigny

17:20
17:30 **Vendor's Event**
Auditorium Alphonse de Lamartine

19:00

20:00 **COMPANY NIGHT:**
Elemental Meinhard PerkinElmer

TUESDAY

08:30 **PLT-1:** A. Makarov

09:15 **KT-1:** K. Marcus

09:40 **PLT-2:** B. Bodenmiller

10:25 **Coffee Break**

11:00	**KT-3:** A. Gundlach-Graham	**KT-2:** M. Montes	**GD WORKSHOP**
11:25	**OT-01:** G. Galbács	**OT-02:** P. Singh	
11:40	**OT-03:** T. Vonderach	**OT-04:** M. Sperling	
11:55	**OT-05:** K. Löschner	**OT-06:** A. Jagielska	
12:10	**OT-07:** G. Stadelmann	**OT-08:** S. López-Sanz	

12:25 **LUNCH BUFFET -** Exhibition Hall
LUNCH SEMINAR - Room Alphand

14:00 **POSTER SESSION**

15:10	**KT-5:** I.Dror	**KT-4:** G. Köllensperger
15:35	**OT-09:** C. Engelhard	**OT-10:** D. Bishop
15:50	**OT-11:** G. Cornelis	**OT-12:** C. Bresson
16:05	**OT-13:** J. Wojcieszek	**OT-14:** S. Mari
16:20	**OT-15:** J. Irrgeher	**OT-16:** R. Alvarez-Fernandez

16:35
16:40 **Heritage lecture:** G. Hieftje
Auditorium Alfred de Vigny

17:20

19:30 **HOT PLASMA PARTY**
Domaine Cinquau
Sponsored by Thermo Fischer Scientific

WEDNESDAY

08:30 **PLW-1:** D. Günther

09:15 **PLW-2:** J. Laserna

10:00 **KW-1:** Ph. Doble

10:25 **Coffee Break**

11:00 **KW-2:** V. Zorba	**KW-3:** J.Feldmann
11:25 **OW-01:** P. Hansen	**OW-02:** B. Meermann
11:40 **OW-03:** R. Buchholz	**OW-02:** D. Pröfrock
11:55 **OW-05:** Van Elteren	**OW-06:** V. Nischwitz
12:10 **OW-07:** B. Wagner	**OW-08:** M. Horvat

12:25 **LUNCH BUFFET -** Exhibition Hall
LUNCH SEMINAR - Rooms Alphand/Monpezat

14:00 **POSTER SESSION**

15:10 **KW-4:** D. Bleiner	**KW-5:** C. Barbante
15:35 **OW-09:** M. Krachler	**OW-10:** E. Vasileva
15:50 **OW-11:** A. Limbeck	**0W-12:** E. Mavrakis
16:05 **OW-13:** A. Carvalho	**OW-14:** N. Sadiq
16:20 **OW-15:** M. Hola	**OW-16:** B. Godlewska

16:35

16:40 **Heritage lecture:** R. Russo
Auditorium Alfred de Vigny

17:20

17:30 **Vendor's event** (room Lautréamont)
Vendor's event (room Alphand)

19:00

20:00 **COMPANY NIGHT :** Agilent

THURSDAY

08:30 **PLTH-1:** J.I. Garcia Alonso

09:10 **KTH-1:** M. Matczuk

09:35 **KTH-2:** M. Foster Mesko

10:05 **KTH-3 :** D. Hare

10:40 **POSTER SESSION**

12:25 **LUNCH BUFFET -** Exhibition Hall
LUNCH SEMINAR - Room Monpezat

14:00 **KTH-4:** Lu Yang	**KTH-5:** A. Okino
14:25 **OTH-01:** T. Prohaska	**OTH-02:** M. Stiborek
14:40 **OTH-03:** Ph. Telouk	**OTH-04:** D. Rosenkranz
14:55 **OTH-05:** M. Bartosiak	**OTH-06:** M. Diehl
15:10 **OTH-07:** J. Vogel	**OTH-08:** C. Hommel
15:35 **OTH-09:** D. Malinovskiy	**OTH-10:** C. Abad
15:50 **OTH-11:** L. Banks	**OTH-12:** W. Goessler

16:05 **Coffee Break**

16:40 **Heritage lecture:** R.S. Houk
Auditorium Alfred de Vigny

17:30 **Young Scientists Career Event** Alphand room

19:00

20:00 **GALA DINER** Salle des Ambassadeurs

FRIDAY

08:30 **PLF-1 :** N. Jakubowski

09:10 **PLF-2:** F. Poitrasson

09:50 **OF-01** J. Kopp

10:05 **OF-02** J. Jimenez-Lamana

10:20 **Coffee Break**

11:00 **OF-03:** W. Lorenc	**OF-04:** M. Moldovan
11:15 **OF-05:**H. Isnard	**OF-06:** Z. Gajdosechova
11:30 **OF-07:** V. Volchek	**OF-08:** F. Chainet
11:45 **OF-09:** I. Komorowicz	**OF-10:** F. Lopez-Linares

12:00 **Closing Ceremony** Auditorium Alfred de Vigny

14:00 **GUIDED VISIT** of the Pau Castle

Detailed programme

Sunday, February 3rd 2019

Registration starts at 8:15	
Short Courses	
09:00 - 12:00	SC-1 Metrology for spectrochemical measurements (E. Bulska)
	SC-2 Nanomaterials (H. Goenaga Infante)
	SC-3 Isotope and isotope dilution ICP MS (J.I. Garcia Alonso)
13:30-16:30	SC-4 ICP MS/MS fundamentals (G. Woods and N. Sugiyama)
	SC-5 Speciation analysis (J. Szpunar)
	SC-6 Laser Ablation ICP MS (D. Günther and B. Hattendorf)
	SC-7 Single Particle and Single Cell Analysis (S. Huynh)

Opening ceremony (Auditorium Alfred de Vigny)	
17:00-17:10	**Welcome** - *Ryszard Lobinski*
17:10-17:15	Address of the Mayor of Pau - *François Bayrou* (or his representative)
17:15-17:25	Address of the President of the University of Pau - *Mohamed Amara* (or his representative)
17:25-17:35	Traditional music from Béarn
17:35-17:50	History of Winter Plasma Conferences - *Ramon Barnes*
17:50-17:55	Winter Plasma Conferences in Pau – 20 years ago and now – *Olivier Donard*
17:55-18:15	Presentations of the conference Platinum sponsors
18:15-18:25	Traditional music from Béarn
18:25-18:45	Special lecture: 'Analytical chemistry: out of the box' - *Freddy Adams*
18:45-19:00	EWCPS-2019 Awards
19:00-19:15	Traditional music of Béarn
	GET-TOGETHER PARTY (Room Henri Faisans Palais Beaumont)

Monday, February 4th 2019

Plenary session: Glow discharge (Auditorium Alfred de Vigny)	
Chair: Gary Hieftje	
08:30-09:15	PLM-1: A. Bengtson - *Past and recent developments in Glow Discharge Optical Emission Spectroscopy (GD-OES)*
09:15-09:40	KM-1: V. Hoffmann - *Light element analysis by analytical glow discharges*
09:40-10:05	KM-2: J. Pisonero - *Current pros and cons of GD-MS and LA-ICP-MS for high spatially resolved elemental analysis*
10:05-10:45	*Coffee break*

Parallel session: Fundamentals (1) (Auditorium Alfred de Vigny)	
Chair: R. Kenneth Marcus	
10:45-11:10	KM-3: T. Iwai - *Development of high-power pulsed microplasma emission source for ultrasmall sample analysis*
11:10-11:25	OM-01: A. Hrdlička - *Multielemental analysis with plasma pencil*
11:25-11:40	OM-03: E. Bolea-Fernandez - *In-cell chemistry to overcome spectral overlap in ICP-MS/(MS): the next step*
11:40-11:55	OM-05: M. Wong- *Electrospray single-cell inductively coupled plasma – mass spectrometry (ES-SC-ICP-MS)*
11:55-12:10	OM-07: I. Gornushkin - *Equilibrium chemistry of boron halides in plasma chemical reactors*
12:10-12:25	OM-09: M. A. Aguirre Pastor - *The use of a multiple inlet nebulizer in ICP-based techniques for spectrochemical analysis*

PARALLEL SESSION: GLOW DISCHARGE (Auditorium Alphonse de Lamartine)	
Chair: Volker Hoffmann	
10:45-11:10	KM-4: Z. Weiss - *Excitation and ionization of iron in argon and neon glow discharges: non-LTE considerations*
11:10-11:25	OM-02: J. Fandiño - *Concentric-electrodes atmospheric pressure glow discharge for the analysis of volatile organic compounds*
11:25-11:40	OM-04: B. Stankov - *Uncovering beryllium line with forbidden component*
11:40-11:55	OM-06: A. Ganeev - *New possibilities of time-of-flight mass spectrometry with pulsed glow discharge in combined hollow cathode*
11:55-12:10	OM-08: L. Lobo - *Quantification strategies for the analysis of major and minor components by means of pulsed Glow Discharge Time-of-Flight Mass Spectrometry*
12:10-12:25	OM-10: V. Brückel - *Mass spectral imaging of iodinated contrast agents in biological tissue samples by means of LA-FAPA-MS*
12:25-14:00	*Lunch* (*Exhibition Hall*) Shimadzu lunch seminar (*room Alphand*) Anton Paar lunch seminar (*room Monpezat*)
14:00-15:10	**Poster sessions** *(salle des Ambassadeurs)* **Fundamentals** (posters MP-1 – MP-44) **Glow Discharge Spectrochemistry** (posters MP-45 – MP-52) **Sample Introduction and Transport Phenomena** (MP-53 – MP-65)

PARALLEL SESSION: SINGLE PARTICLE ANALYSIS (1) (Auditorium Alfred de Vigny)	
Chair: Jan Preisler	
15:10-15:35	KM-5: H. Goenaga Infante - *The power of micro-second detection ICP-MS for the accurate determination of nanoparticle number concentration: Underpinning metrology for biomedical applications*
15:35-15:50	OM-11: F. Laborda - *About detectability and detection limits in single particle ICP-MS*
15:50-16:05	OM-13: K. Inagaki - *Multi-spray CGrid nebulizer for perfect matrix-matching in single-particle ICP-MS*
16:05-16:20	OM-15: D. Mozhayeva - *A novel data processing strategy for quantification of nanoparticles and dissolved metals in mixtures with SP-ICP-MS and microsecond time resolution*
16:20-16:35	OM-17: K. Chun - *Double-Viewing-Position SP-ICP-AES*

Parallel session: Metallomics (1) (Auditorium Alphonse de Lamartine)	
Chair: Joanna Szpunar	
15:10-15:35	KM-6: J. Ruiz - *New advances in the absolute quantification of biomolecules using ICP MS/MS and generic standards*
15:35-15:50	OM-12: A. Raab - *Pros and cons for the use of ICP-MS in proteomics*
15:50-16:05	OM-14: T. Garcia-Barrera - *Selenometabolites and selenoproteins mother-offspring transfer through human breast milk and cord serum by column switching ICP triple quadrupole MS*
16:05-16:20	OM-16: C. Swart - *Potential reference measurement procedures to quantify metalloproteins in CSF and serum*
16:20-16:35	OM-18: L. Ouerdane - *Screening of metallophores content and metal transport in microorganisms by the use of isotopically enriched species*

Plenary session: Heritage lecture (Auditorium Alfred de Vigny)	
Chair: Freddy Adams	
16:40-17:20	A. Montaser - *Mating with an elephant in atomic spectrometry*

Vendor's event (Auditorium Alphonse de Lamartine)	
17:30-19:00	Agilent Workshop

Company Night:	• **Elemental Meinhard** • **PerkinElmer**

Tuesday, February 5th 2019

Plenary session: New horizons of plasma spectrometry (1)
(Auditorium Alfred de Vigny)

Chair: Norbert Jakubowski

08:30-09:15	PLT-1: A. Makarov - *Orbitrap analyzer and plasma ion sources: could they work together?*
09:15-09:40	KT-1: K. Marcus - *Coupling of the liquid sampling-atmospheric pressure glow discharge to Orbitrap mass analyzers: changing the way we look at plasma source mass spectrometry*
09:40-10:25	PLT-2: B. Bodenmiller - *Highly multiplexed imaging of tissues with subcellular resolution by imaging mass cytometry*
10:25-11:00	*Coffee break*

Parallel session: Single particle analysis (2) (Auditorium Alphonse de Lamartine)

Chair: Heidi Goenaga Infante

11:00-11:25	KT-3: A. Gundlach-Graham - *Monte Carlo simulations to characterize low-count-rate signals in ICP-TOFMS and applications to single-particle analysis*
11:25-11:40	OT-01: G. Galbács - *Analytical method development for nanoparticle characterization by SP ICP-MS: beyond monometallic spherical particles*
11:40-11:55	OT-03: T. Vonderach - *Analysis of single cells transported via microdroplets using ICP-TOFMS*
11:55-12:10	OT-05: K. Löschner - *Analysis of titanium dioxide nanoparticles in food by triple quadrupole and high resolution ICP-MS in single particle mode*
12:10-12:25	OT-07: G. Stadelmann - *Determination of total uranium amount in single particles by ID-MC-ICP-MS for characterization of particle reference materials*

PARALLEL SESSION: METALLOMICS (2) (Auditorium Alfred de Vigny)	
Chair: Gunda Köllensperger	
11:00-11:25	KT-2: M. Montes - *The combination of labelled antibodies and ICP-MS for biomarker analysis: recent progress and remaining challenges for multiplexing*
11:25-11:40	OT-02: P. Singh - *Quantification of breast cancer biomarkers using immune histochemically assisted imaging by LA-ICP-MS*
11:40-11:55	OT-04: M. Sperling - *Gadolinium retention in the human body following administration of gadolinium-based contrast agents: information obtained by elemental bioimaging*
11:55-12:10	OT-06: A. Jagielska - *Dependence of LA-ICP-MS results on the preparation of biological and clinical samples*
12:10-12:25	OT-08: S. López-Sanz - *Hydrodynamic separation techniques coupled ICP-MS for characterization of gold nanoparticles and dissolved gold species in in- vitro toxicological assays*
12:25-14:00	*Lunch (Exhibition Hall)* Agilent lunch seminar (*room Alphand*)
14:00-15:10	**POSTER SESSIONS** (*Salle des ambassadeurs*) **Environmental and Geological Analysis** (posters TP-1 – TP-49) **Nanomaterial Analysis** (posters TP-50 – TP-71)

PARALLEL SESSION: NANOPARTICLE/ENVIRONMENTAL ANALYSIS (Auditorium Alphonse de Lamartine)	
Chair: Francisco Laborda	
15:10-15:35	KT-5: I. Dror - *Detection and characterization of nanoparticles in soil-water plant environments*
15:35-15:50	OT-09: C. Engelhard - *ICP-MS with microsecond time resolution: on recent improvements and the detection of nanoparticles in environmental waters*
15:50-16:05	OT-11: G. Cornelis - *Laser ablation coupled to SP ICP-MS can quantify size and number concentration of inorganic nanomaterials in soils*
16:05-16:20	OT-13: J. Wojcieszek - *Model studies of the uptake and behaviour of CeO2 nanoparticles in radish* (Raphanus sativum L.*) using mass spectrometry techniques*
16:20-16:35	OT-15: J. Irrgeher - *Technology-critical elements (TCEs): Source characterization and assessment of environmental exposure*

PARALLEL SESSION: METALLOMICS (3) (Auditorium Alfred de Vigny)	
Chair: Maria Montes-Bayon	
15:10-15:35	KT-4: G. Köllensperger - *Novel workflows for metal-based anticancer drug research enabled by ICP-TOF-MS*
15:35-15:50	OT-10: D. Bishop - *Quantitative imaging of dystrophin using immunohistochemical-assisted imaging-mass spectrometry*
15:50-16:05	OT-12: C. Bresson - *Investigation of uranium effects on neuron-like cells: an interdisciplinary analytical approach*
16:05-16:20	OT-14: S. Mari - *The use of plasma-assisted techniques to unravel the genetics of metal storage in seeds*
16:20-16:35	OT-16: R. Alvarez-Fernandez - *Single cell analysis of selenized yeast using triple quadrupole ICP-MS*

PLENARY SESSION: HERITAGE LECTURE (Auditorium Alfred de Vigny)	
Chair: Detlef Günther	
16:40-17:20	G. Hieftje - *And now what? (Reprise)*
19:30-24:00	**HOT PLASMA PARTY** sponsored by Thermo Fischer Scientific **(*Domaine Cinquau*)**

Wednesday, February 6th 2019

Plenary session: Laser-assisted plasma spectrometry (Auditorium Alfred de Vigny)	
Chair: Rick Russo	
08:30-09:15	PLW-1: D. Günther - *Contributions to automated element imaging by Laser Ablation ICP-Mass Spectrometry*
09:15-10:00	PLW-2: J. Laserna - *Laser-induced breakdown spectroscopy: the secret life of surfaces and other captivating insights*
10:00-10:25	KW-1: Ph. Doble - *Atomic oncology: personalising cancer radiation treatments with LA-ICP-MS*
10:25-11:00	*Coffee break*

Parallel session: Laser ablation and LIBS (1) (Auditorium Alfred de Vigny)	
Chair: Philip Doble	
11:00-11:25	KW-2: V. Zorba - *New and emerging femtosecond laser sampling approaches in laser induced breakdown spectroscopy*
11:25-11:40	OW-01: P. Hansen - *Simple modeling of LIBS plasma parameters for extraterrestrial applications*
11:40-11:55	OW-03: R. Buchholz - *^{57}Fe-enriched iron oxide nanoparticles – long term fate and cell tracking determined by LA-ICP-MS and MRI*
11:55-12:10	OW-05: J. van Elteren - *Rules of thumb for fast and high-quality LA-ICPMS imaging in single pulse or continuous scanning mode*
12:10-12:25	OW-07: B. Wagner - *Laser ablation ICP MS for analytical recycling of iron-gallium ink indicator papers*

Parallel session: Environmental analysis (1) (Auditorium Alphonse de Lamartine)	
Chair: Carlo Barbante	
11:00-11:25	KW-3 J. Feldmann - *Elemental speciation in biological and environmental samples involves natural nanoparticles and molecular species*
11:25-11:40	OW-02: B. Meermann - *An automated single algae-ICP-ToF-MS approach for the investigation of metal uptake in single diatoms*
11:40-11:55	OW-04: D. Pröfrock - *Assessing legacy pollution and new inorganic contaminants in complex environmental samples using ICP-MS based techniques*

11:55-12:10	OW-06: V. Nischwitz - *Improving mass balance for size resolved elemental speciation of environmental water samples using FFF online with ICP-MS*
12:10-12:25	OW-08: M. Horvat - *Traceability of oxidized mercury measurements in air*
12:25-14:00	*Lunch (Exhibition Hall)* Elemental Meinhard lunch seminar (room Monpezat) Thermo Fisher Scientific lunch seminar (room Alphand)
14:00-15:10	**Poster sessions** *(salle des Ambassadeurs)* **Imaging and Bioimaging** (posters WP-1 - WP-20) **Laser Ablation of Plasma Spectrochemistry** (WP-21 – WP-35) **Laser-Induced Breakdown Spectroscopy** (WP-36 – WP-45) **Biological and Clinical Analysis** (WP-46 – WP-73)

PARALLEL SESSION: LASER ABLATION AND LIBS (2) (Auditorium Alfred de Vigny)

Chair: Johannes van Elteren

15:10-15:35	KW-4: D. Bleiner - *Laser ablation 3D chemical mapping with X-ray lasers*
15:35-15:50	OW-09: M. Krachler - *Quantitative assessment of spatial inhomogeneity of major and minor uranium isotopes in solid nuclear materials using LA-MC-ICP-MS*
15:50-16:05	OW-11: A. Limbeck - *Development of laser based procedures for stoichiometry analysis of ternary boride thin films*
16:05-16:20	OW-13: A. Carvalho - *Multi-energy calibration and sample fusion as alternatives for quantitative analysis of high silicon content samples by LIBS*
16:20-16:35	OW-15: M. Hola - *Feasibility of Nanoparticle-Enhanced Laser Ablation Inductively Coupled Plasma MS*

PARALLEL SESSION: ENVIRONMENTAL ANALYSIS (2) (Auditorium Alphonse de Lamartine)

Chair: Jörg Feldmann

15:10-15:35	KW-5: C. Barbante - *Mass spectrometry under the ice*
15:35-15:50	OW-10: E. Vasileva - *Monitoring of priority and emerging contaminants in the open ocean*
15:50-16:05	OW-12: E. Mavrakis - *Investigating arsenate uptake in C. reinhardtii cells using Single Cell ICP-MS and its effect on lipid remodelling using ambient MS*

16:05-16:20	OW-14: N. Sadiq - *You've got to be kelping me! Determination of $^{129}I/^{127}I$ in kelp samples using ICP-MS/MS*
16:20-16:35	OW-16: B. Godlewska-Żyłkiewicz - *Studies of biosorption of nano and ionic forms of gold by green algae in surface water by HPLC-ICP MS*

PLENARY SESSION: HERITAGE LECTURE (Auditorium Alfred de Vigny)	
Chair: Javier Laserna	
16:40-17:20	R. Russo - *A career history of laser ablation for chemical analysis*

VENDOR'S EVENT	
17:30-19:00	ETV User Club arranged by SPECTRO (AMETEK) (*room Lautréamont)*
17:30-19:00	Horiba Users Meeting *(room Alphand)*

	COMPANY NIGHT: Agilent

Thursday, February 7th 2019

Plenary session: Award session (Auditorium Alfred de Vigny)	
Chair: Ryszard Lobinski	
08:30-09:10	**PLTH-1: Agilent European Plasma Spectrochemistry Awardee:** J.I. Garcia Alonso - *A paradigm change in isotopic measurements by Mass Spectrometry: isotope abundances, molar fractions and linear regression calculations*
09:10-09:35	**KTH-1: Agilent Rising Star in Plasma Spectrochemistry Awardee**: M. Matczuk - *Joint forces of ICP-MS-based techniques for effective examination of the intracellular processing of gold nanoparticles*
09:35 -10:05	**KTH-2: JAAS Emerging Investigator Lecture**: M. Foster Mesko - *Green sample preparation methods for further determination of metals and non-metals by atomic spectrometric techniques*
10:05-10:40	**KTH-3 Emerging Leader in Atomic Spectroscopy Awardee**: D. Hare - *Atomic pathology: The past, present and future of elemental imaging in medical research*
10:40- 12:25	**Poster sessions** **Stable Isotope Analysis** (posters THP1 – THP-69) **Advanced Materials and Industrial Analysis** (THP-70 – THP-81) **Petroleum and Semiconductor Materials** (THP-82 – THP-86)
12:25-14:00	*Lunch (Exhibition Hall)* PerkinElmer lunch seminar (*room Monpezat*)

Parallel session: Isotope ratio analysis (Auditorium Alfred de Vigny)	
Chair: José Ignacio Garcia Alonso	
14:00-14:25	KTH-4: Lu Yang - *Absolute isotope amount ratio measurements by MC-ICP MS*
14:25-14:40	OTH-01: T. Prohaska - *The isotopic challenge: metrological approaches for accurate isotope measurements*
14:40-14:55	OTH-03: Ph. Telouk - *Copper isotopic composition as a biomarkers for liver cancer : a large cohort study*
14:55-15:10	OTH-05: M. Bartosiak - *Determination of Fe isotopic composition using MC-ICP-MS for the elucidation of the iron uptake mechanisms in yeast mutants*
15:10-15:35	OTH-07: J. Vogel -*Triple isotope fractionation exponents of elements measured by MC-ICP-MS - an example of Mg*

15:35-15:50	OTH-09: D. Malinovskiy - *Accurate determination of lithium and boron isotope ratios by MC-ICP-MS with normalisation to an internal standard*
15:50-16:05	OTH-11: L. Banks - *Developing low-volume solution ICP-MS for high-precision uranium isotope analysis*

PARALLEL SESSION: FUNDAMENTALS (2) (Auditorium Alphonse de Lamartine)	
Chair: Kazumi Inagaki	
14:00-14:25	KTH-5: A. Okino - *Non-contact mass spectrometry of adhesive compounds on heat-sensitive surface using temperature-controllable plasma jet*
14:25-14:40	OTH-02: M. Stiborek - *Cold Plasma: way to improve repeatability of metal analysis in sub-microliter volumes?*
14:40-14:55	OTH-04: D. Rosenkranz - *Matrix matched validation procedure for single cell measurements with automized µ-flow injection*
14:55-15:10	OTH-06: M. Evertz - *Plasma-based techniques: a versatile tool to gather insights into lithium losses of lithium ion batteries*
15:10-15:35	OTH-08: C. Hommel - *Optimization possibilities for difficult matrices with ETV-ICP OES*
15:35-15:50	OTH-10: C. Abad - *Critical evaluation of optical spectrometry vs mass spectrometry for stable isotope analysis*
15:50-16:05	OTH-12: W. Goessler - *Changes of size-resolved element distributions in particulate matter induced by New Year's Eve fireworks*
16:05-16:40	*Coffee break*

PLENARY SESSION: HERITAGE LECTURE (Auditorium Alfred de Vigny)	
Chair: Ramon Barnes	
16:40-17:30	R.S. Houk - More misnomers, misconceptions, and musings in ICP spectroscopy
17:30-19:00	Young Scientists Career Event (*Alphand room*)
20:00	**GALA DINNER** *(Salle des Ambassadeurs)*

Friday, February 8th 2019

Plenary session: New horizons of plasma spectrometry (2) (Auditorium Alfred de Vigny)

Chair: Thomas Prohaska

08:30-09:10	PLF-1: N. Jakubowski - *Method development for single cell analysis by use of ICP-MS and ICP-TOFMS*
09:10-09:50	PLF-2: F. Poitrasson - *Exploring adventure in the land of MC-ICP-MS*
09:50-10:05	OF-01: J. Kopp - *Trace element profiling in very small volumes of human serum for the application in large cohorts*
10:05-10:20	OF-02: J. Jimenez-Lamana - *Nanoplastics, the new threat to environmental waters: how can ICP-MS help to address this issue ?*
10:20-11:00	*Coffee break*

Parallel session: Elemental speciation (Auditorium Alfred de Vigny)

Chair: Ewa Bulska

11 :00-11 :15	OF-03: W. Lorenc - *Study of speciation of As, Cr and Sb in bottled flavored and functional drinking water samples using advanced analytical techniques IEC/SEC-HPLC/ICP-DRC-MS and ESI-MS^n*
11:15-11:30	OF-05: H. Isnard - *Hyphenation between capillary electrophoresis and multi collector inductively coupled plasma mass spectrometry for isotope ratio measurements*
11:30-11:45	OF-07: V. Volchek - *The use of hyphenated techniques (CZE-ICP-MS, HPLC-ICP-OES) for the study of inorganic complexes*
11:45-12:00	OF-09: I. Komorowicz - *Arsenic speciation analysis in liquid and solid samples by hyphenated technique HPLC/ICP-DRC-MS*

Parallel session: Petroleum analysis (Auditorium Alphonse de Lamartine)

Chair: Zofia Kowalewska

11:00-11:15	OF-04: M. Moldovan - *Determination of sulfur-containing compounds in crude oil products by GC-ICP-MS/MS*
11:15-11:30	OF-06: Z. Gajdosechova - *Headspace analysis of Hg in petroleum hydrocarbons*
11:30-11:45	OF-08: F. Chainet - *Speciation of trace contaminants in the refinery industry using gas chromatography coupled to ICP-MS/MS*

11:45-12:00	OF-10: F. Lopez-Linares - *Application of Single Particle Inductively Coupled Plasma-Mass Spectrometry (sp-ICP-MS) in the petroleum industry*

PLENARY SESSION (Auditorium Alfred de Vigny) - Closing ceremony
Closing remarks - *Ryszard Lobinski*
EWCPS-2019 Poster Awards
Invitation to the EWCPS-2021 - *Johannes van Elteren*

14:00-	Guided visit of Pau Castle

Posters – Monday, February 4th

Fundamentals

MP-1 **Study on carbon-induced signal enhancement in ICP MS: an approach from a spatial distribution of analyte signal intensities in the plasma** - Tomoko Ariga, Yanbei Zhu, Kazumi Inagaki

MP-2 **Advantages of sophisticated sample introduction accessories for the trace element analysis of wear metals in organic sample matrices by ICP OES** - Sanja Asendorf, Nora Bartsch, Sebastian Weyermann

MP-3 **Capabilities and performance of quadrupole based LA ICP MS** - Dhinesh Asogan, Daniel Kutscher

MP-4 **Ultra trace analysis of noble metals in rock samples using triple quadrupole ICP MS** - Dhinesh Asogan, Daniel Kutscher

MP-5 **Multielement analysis of coolant and antifreeze products using ICP OES** - Nora Bartsch, Sanja Asendorf, Sebastian Weyermann

MP-6 **Simultaneous quantification od iodine and other elements relevant for high level nuclear waste under acidic conditions via ICP MS for determination of sorption isotherms on Ca-bentonite** - Kristina Brix, Ralf Kautenburger, Christina Hein, Jonas Sander, Guido Kickelbick

MP-7 **Electrochemistry coupled to flowing atmospheric pressure afterglow mass spectrometry for metabolism studies of polycyclic aromatic hydrocarbons** - Valerie Bruckel, Michael Sperling, Uwe Karst

MP-8 **Revolutionizing sample preparation for trace metal analysis with single reaction chamber (SRC) microwave digestion** - Giulio Colnaghi, Gianpaolo Rota, Diego Carnaroglio

MP-9 **Accurate LA-ICP MS analysis of mineral phases using non-matrix matched reference materials** - Leonid Danyushevsky, Jay Thompson, C Ashley Norris

MP-10 **Application of a transient ICP MS measurement for samples with high salinity** - Christina Hein, Kristina Brix, Ralf Kautenburger

MP-11 **Speciation of phosphorous-based decomposition products in lithium ion battery electrolytes by HPLC ICP-SF-MS** - Jonas Henschel, Yannick Stenzel, Martin Winter, Sascha Nowak

MP-12 **Development of a microwave-assisted digestion protocol for trace metal analysis in different types of polymers using ICP MS/MS** - Lars Hildebrandt, Tristan Zimmermann, Anna Reese, Daniel Proefrock

MP-13 **High performance ICP MS plasma consuming ½ of argon. Standard Fassel torch, robust, high matrix tolerant.** - Iouri Kalinitchenko, Martin Gleisner, Wolfram Weisheit, Rene Chemnitzer, Margrit Killenberg

MP-14 **Particle analysis of lithium ion battery materials** - Till-Niklas Kroger, Simon Wiemers-Meyer, Martin Winter, Sascha Nowak

MP-15 **A chemometric approach to access doubly charged and oxide formations and sensitivity for USP < 232> elements on liquid drug samples using aerosol dilution for ICP MS** - Rodolfo Lorencatto, Gabriel Gustinelli Arantes De Carvalho, Pedro Vitoriano De Oliveira

MP-16 **Development of an oyster tissue certified reference material for the analysis of total mercury and its use in proficiency testing** - Jong Wha Lee, Hwijin Kim, Euijin Hwang, Jwahaeng Park, Sung Woo Heo, Yong- Hyeon Yim, Youngran Lim, Myung Chul Lim, Kyoung-Seok Lee

MP-17 **Barrier Ionization Discharge (BID) detector – A powerful GC detector to quantify permanent gases and light hydrocarbons, evolved from lithium ion batteries** - Marco Leising, Fabian Horsthemke, Martin Winter, Sascha Nowak

MP-18 **High sensitivity, fast scanning, sector field ICP MS – Improving sensitivity for laser ablation with the Jet interface** - Torsten Lindemann, Joachim Hinrichs, Grant Craig, Johannes Schwieters

MP-19 **Multi-energy and multi-isotope calibration: strategies for the determination of nutrients and contaminants in meat by ICP-OES and ICP MS** - Julymar Marcano, Ana Beatriz Santos Silva, Ana Rita Araujo Nogueira

MP-20 **Comparison of 193 nm and 266 nm wavelengths for elemental bio-imaging by laser ablation inductively coupled plasma** - Katherine Mclachlin, Leif Summerfield, Robert Hutchinson, David Douglas, Ciaran O'Connor

MP-21 **Using triple quadrupole ICP MS in routine analysis of environmental and food samples** - Simon Nelms, Daniel Kutscher

MP-22 **Overcoming the challenges in pharmaceutical analyses, with a focus on OTC allergy tablet analysis with ICP OES** - Kenneth Neubauer, Erica Cahoon

MP-23 **Ultra-high precision with ICP OES using continuous real-time simultaneous internal standardization** - Kenneth Neubauer, Wim Van Bussel, Erica Cahoon

MP-24 **Comprehensive software for data reduction of LA-ICP MS data sets** - Ashley Norris, Leonid Danyushevsky

MP-25 **Flat capillary solution cathode glow discharge: a useful modification for improved analytical performance and fundamental characterization.** - Jaime Orejas, Nicholas Hazel, Andrew Schwartz, Steven Ray

MP-26 **Characterization and evaluation of a surface wave plasma as an ionization source for mass spectrometry -** Jaime Orejas, Ludovic Sudrie, Juslan Lo, Laurent Therese, Louis Latrasse, Philippe Guillot

MP-27 **Quantitative and qualitative analysis of liquid samples by spatial heterodyne Raman spectroscopy -** David Palasti, Ardian Gojani, Gabor Galbacs, Igor Gornushkin

MP-28 **A novel calibration strategy for the accurate quantification of elemental species using HPLC-ICP MS -** Panayot Petrov, Heidi Goenaga Infante

MP-29 **Improving laboratory efficiency with a combined prepFAST and chromatography method for chromium speciation -** C Derrick Quarles Jr, Michael Szoltysik, Patrick Sullivan, Maurice Reijnen

MP-30 **Inline sample preparation system for micro volume clinical samples -** C Derrick Quarles Jr, Stephen Sudyka, Austin Schultz, M. Paul Field, Daniel Wiederin

MP-31 **Automated laser ablation sampling for food safety -** C Derrick Quarles Jr, Todor Todorov, Ciaran O'Connor, Rob Hutchinson, Katherine Mclachlin

MP-32 **Advantages of inline dilution for LC-ICP MS based applications involving arsenic speciation -** C Derrick Quarles Jr, Patrick Sullivan, M. Paul Field, Daniel Wiederin

MP-33 **High-performance LA-ICP TOF MS imaging combining the Cobalt LA cell and ICP TOF -** Martin Rittner, Ciprian Stremtan

MP-34 **Using multi-lines post-analysis data processing for the enhancement of ICP-OES performances** Cedric Rivier, Sarah Baghdadi, Marielle Crozet, Jean-Luc Dautheribes, Sophie Gracia, Sebastien Picart

MP-35 **Space charge effect behind hyperskimmer in ICP MS -** Serguei Savtchenko, Hamid Badiei, Bohdan Atamanchuk, Dickson Cheung, Paul Farnsworth, Jessica Larsen

MP-36 **Recent advances in detection, quantification and population distribution of single and dual analytes in single cell and single particle ICP MS -** Stephan Chady, Ruth Merrifield, Samad Bazargan

MP-37 **Applications of dual analyte analysis of metals in single - particle and single cell ICP MS -** Stephan Chady, Ruth Merrifield, Samad Bazargan

MP-38 **Application ICP MS and ICP-OES for measurement of trace elemental impurities and certified target value in CRM -** Tatiana Stolboushkina, Aleksei Stakheev, Vladimir Dobrovolskiy

MP-39 **The effect of instrument sensitivity on sample throughput -** Eike Thamm, Iouri Kalinitchenko

MP-40 **Determination of nanoparticles using ICP MS -** Eike Thamm, Peio Riss

MP-41 **Improvements in the determination of uncertainties of isotopic ratios for uranium samples thanks to IAEA Round Robin** - Olivier Vigneau, Nadege Arnal, Christophe Winkelmann

MP-42 **Solving doubly charged ion interferences using ICP MS/MS with nitrous oxide -** Naoki Sugiyama

MP-43 **Uses of Agilent 8900 ICP MS/MS for nuclear applications -** Alain Desprez

MP-44 **Improvement of the nanoparticle size limit of detection for SP-ICP-MS using a desolvating nebuliser and peak detection algorithm optimisation to distinguish small particles from ionic background with the HR-ICP-MS Attom -** Ariane Donard, Phil Shaw,Madjid Hadioui, K. Newman

Glow Discharge Spectrochemistry

MP-45 **A new approach for effective ionisation of elements with high ionisation potential such as fluorine and oxygen in pulsed glow discharge mass spectrometry with using a neon plasma -** Viktoriia Chuchina, Alexander Ganeev, Anna Gubal, Nikolay Solovyev, Yegor Lyalkin, Oleg Glumov, Viktor Yacobson

MP-46 **Deciphering the lithium ion movement in lithium ion batteries: determination of the isotopic abundances of 6Li and 7Li -** Marcel Diehl, Sascha Nowak, Martin Winter

MP-47 **Application of glow discharge mass spectrometry for analyzing Si/C-composite anodes for lithium ion batteries – determining the influence of the state of charge and dry film thickness -** Marcel Diehl, Karina Ambrock, Alex Friesen, Sascha Nowak, Martin Winter

MP-48 **Fast analysis of direct injected gaseous samples using radiofrequency pulsed glow discharge time-of-flight mass spectrometry -** Jonatan Fandino, Marcos Bouza, David Blanco, Alfredo Sanz-Medel, Jorge Pisonero, Nerea Bordel

MP-49 **Direct quantification of high-ionisation energy elements by pulsed glow discharge mass spectrometry – a study of different discharge gases -** Anna Gubal, Alexander Ganeev, Viktoriia Chuchina, Nikolay Solovyev, Ilja Gorbunov, Oleg Glumov, Viktor Yacobson

MP-50 **Gallium analysis using s-pulsed fast flow glow discharge mass spectrometry -** Joachim Hinrichs, Torsten Lindemann, Johannes Schwieters

MP-51 **Analysis of highly boron-doped diamond thin films: comparison of GD-OES, SIMS and Raman spectroscopy -** Zdenek Weiss, Petr Ascheulov, Andrew Taylor, Jan Lorincik, Matvei Aleshin, Vincent Mortet

MP-52 **Spatially-resolved glow discharge mass spectrometry analysis -** Piotr Konarski, Joachim Ażgin, Maciej Miśnik, Aleksander Zawada

Sample Introduction and Transport Phenomena

MP-53 **Direct analysis of gold and silver nanoparticles of different sizes from dried droplets using substrateassisted laser desorption single particle ICP MS -** Jakub Bělehrad, Marek Stiborek, Jan Preisler

MP-54 **Development of a low dispersion laser chamber for ultra-fast, automated imaging of biological and geological materials -** David N. Douglas, Leif Summerfield, Shane Hilliard

MP-55 **Coupling digital microfluidics with ICP MS for single nanoparticle or cell analysis -** Valerie Geertsen, Theo Jourdain, Florent Malloggi

MP-56 **Using online-LASIL for stoichiometry determination of Fe doped SrTiO3 thin films -** Christopher Herzig, Johannes Frank, Maximilian Morgenbesser, Alexander K. Opitz, Jurgen Fleig, Andreas Limbeck

MP-57 **Isotopic, multi-elemental and nanoparticle microanalysis with a new micro-flow uptake device for direct injection nebulization in ICP MS -** Pascale Louvat, Mickael Tharaud, Matthieu Buisson, Claire Rollion-Bard, Marc Benedetti

MP-58 **Online microdroplet calibration for size and concentration determination of nanoparticle mixtures by ICP-TOF-MS -** Kamyar Mehrabi, Detlef Gunther, Alexander Gundlach-Graham

MP-59 **Applications of FFF combined with ICP MS to nanoparticle and colloid measurements in the environment -** Robert Reed, James Ranville, Angie Barber, Chad Cuss

MP-60 **Single-cell analysis enabled by ICP-TOF-MS -** Anna Schoeberl, Sophie Neumayer, Andreas Schweikert, Gerrit Hermann, Sarah Theiner, Gunda Koellensperger

MP-61 **Development of a new direct injection nebulizer for single-particle/cell ICP MS -** Miyashita Shin-Ichi, Fujii Shin-Ichiro, Inagaki Kazumi

MP-62 **Stable and radiogenic isotope ratio measurements of cave and marine coral samples using multicollector ICP MS with a desolvating nebulizer sample introduction accessory -** Fred Smith, Damon Green, Victor Polyak

MP-63 **High volume in-line syringe dilution system for ICPOES and ICP MS -** Andrew Toms, Austin Schultz, Daniel Wiederin

MP-64 **Automated preconcentration and matrix removal for ultratrace determination of radium in environmental waters -** Nathan Saetveit, Aurelien Viscardi

MP-65 **Weighted averaging based spectrum processing scheme for skin cancer detection based on laser-Induced breakdown spectroscopy measurements -** Ekta Srivastava, Euiseok Hwang , Sungho Jeong, Janghee Choi

Posters - Tuesday, February 5th

Environmental and Geological Analysis

TP-1 **Assessment of hyperaccumulation of selected metals by native plants growing in polluted Peruvian post-mining areas -** Edith Maricela Cruzado Tafur, Lisard Torro I Abat, Katarzyna Bierla, Joanna Szpunar

TP-2 **Examination of heavy metal contamination found in raisins, sultanas and currants by ICP-MS** Patricia Atkins, Elaine Hasty

TP-3 **Contamination, adulteration and counterfeiting: an examination of sources and concentrations of heavy metals present in food, spices, beverages and drinking water -** Patricia Atkins

TP-4 **Examination of elemental composition and toxic metals in bread spreads -** Patricia Atkins, Elaine Hasty

TP-5 **Tracing source and mobility of metals and metalloids in a hydrosystem impacted by past mining activities (Morelos state, Mexico) -** Aurelie Barats, Christophe Renac, Anna Maria Orani, Gael Durrieu, Humberto Saint Martin, Marisa Vicenta Esteller, Sofia Garrido Hoyos

TP-6 **U-Pb dating of carbonates by fs-LA-ICP-MS -** Fanny Claverie, Guilhem Hoareau, Christophe Pecheyran, Olivier Chailan, Jean-Pierre Girard

TP-7 **Determination of trace metals and organometals (Hg, Sn) in high altitude lake waters of the Pyrenees -** Bastien Duval,2, Emmanuel Tessier, Alberto De Diego, Arana Gorka, Olaia Linero, David Amouroux

TP-8 **Development of complementary CE-MS methods for speciation analysis of metal based antifouling biocides in surface water -** Sebastian Fasbender, Ann-Katrin Doring, Björn Meermann

TP-9 **Trace- and ultra-trace analysis of high mineralized ground waters -** Lisa Fischer, Stephan Hann

TP-10 **Trace metals in particulate matter emitted by marine engines – potential environmental and health impact-** Zuzana Gajdosechova, Martin Couillard, Joel Corbin, Stéphanie Gagne

TP-11 **Speed up your productivity - High throughput measurement of drinking water -** Martin Gleisner

TP-12 **Reliability of the direct ICP-MS analysis of volcanic ash nanoparticles -** Alexandr Ivaneev, Stephane Faucher, Natalia Fedyunina, Vasily Karandashev, Mikhail Ermolin, Petr Fedotov, Gaetane Lespes

TP-13 **Palladium determination after solid phase extraction on strongly basic anion resins -** Katarzyna Kińska, Monika Sadowska, Joanna Kowalska, Beata Krasnodębska-Ostręga

TP-14 **Development and validation of analytical procedures for reference measurements of mercury in marine environment compartments with direct and species specific isotope dilution analysis and hyphenated ICPMS techniques -** Agnieszka Krata, Emiliya Vasileva-Veleva, Marcin Wojciechowski, Ewa Bulska

TP-15 **Determination of methylmercury using liquid chromatography – photochemical vapour generation – atomic fluorescence spectroscopy (LC-PVG-AFS) – A comparison with ICP-MS** - Shaun Lancaster, Joerg Feldmann, Eva Krupp, Warren Corns

TP-16 **Quantitative analysis of Pb in soils in multimedia environment using fsLA and ICP-MS** - Min Young Lee, Sung Hwa Choi, Eun Ji Kim, Yu Ri Lee, Eun Mi Choi, Kyung Su Park

TP-17 **Application of ICP-MS/MS for determination of chromium in environmental matrices** - Barbara Leśniewska, Beata Godlewska-Żyłkiewicz

TP-18 **Determination of major and trace elements in geological samples by laser ablation solution sampling inductively coupled plasma mass spectrometry -** Xiuhong Liao, Zhaochu Hu

TP-19 **Laser ablation inductively coupled plasma mass spectrometry for the quantitative analysis of pellets of plant materials -** Pierre Masson, Thierry Dalix

TP-20 **Biomonitoring of titanium contamination in moss samples by ICP-OES -** Pierre Masson, Patrice Soule

TP-21 **Determination of heavy metals in certified fish samples using ICP-mass spectrometry** - Uwe Oppermann, Ludivine Fromentoux, Pravin Konde, Joyce Lim

TP-22 **Quantitative analysis of contaminants in beverages using ICP-mass spectrometry** - Uwe Oppermann, Jan Knoop, Johannes Hesper

TP-23 **Temporal variation of priority and emerging contaminants in sediment core from Kiel Bay, western Baltic sea -** Anna Maria Orani, Emiliya Vasileva-Veleva

TP-24 **Distribution of Se in French forest ecosystems compartments -** Paulina Pisarek, Maïte Bueno, Yves Thiry, Manuel Nicolas, Herve Gallard 4, Isabelle LeHecho

TP-25 **Method development aiming at the determination of mineral nutrients in vegetable tissues by MIP-OES to underpin agricultural research -** Daiane Placido Torres, Adilson Bamberg, Carlos Posser Silveira

TP-26 **Analysis of wines by ICP-MS using TotalQuant -** Ewa Pruszkowski

TP-27 **Accurate analysis of seawaters by HR-ICP-OES and ICP-MS -** Peio Riss, Lionel Lumet

TP-28 **Corrosion protection of offshore wind farms: a new - potential source of inorganic contaminants for the marine environment ? -** Anna Reese, Nathalie Voigt, Tristan Zimmermann, Johanna Irrgeher , Daniel Profrock

TP-29 **Optimization of a HPLC mixed-mode column methodology coupled to ICP-MS for selenium speciation in natural waters -** Andrea Romero Rama, David Amouroux, Maite Bueno

TP-30 **Seasonal variations on dissolved selenium speciation in Lake Kinneret -** Andrea Romero Rama, Yaron Be'eri-Shlevin, Assaf Sukenik, Maïte Bueno, Emmanuel Tessier, David Amouroux

TP-31 **ICP-OES assessment of silver distribution in plant material after exposure to capped Ag-NPs -** Sanda Rončević, Ivan Nemet, Petra Peharec Štefanić, Zrinka Gale, Bernardo Marciuš

TP-32 **Determination of trace, minor and major elements in steel using the PlasmaQuantMS® -** Rui Santos

TP-33 **PlasmaQuantMS®: a precise, accurate and versatile tool -** Rui Santos

TP-34 **Stability of silver-based nanoparticles at environmentally relevant concentrations in seawater monitored by SP-ICP-MS -** Alexander Urstoeger, Andreas Wimmer , Michael Schuster

TP-35 **Asymmetric flow field-flow fractionation (AF4) ICP-MS studies of the sorption of lead on nanoplastics -** Cloé Veclin, Anne-Catherine Pierson-Wickmann, Julien Gigault, Melanie Davranche, Hind El Hadri, Stephanie Reynaud, Bruno Grassl, Elise Deniau, Javier Jimenez-Lamana, Joanna Szpunar

TP-36 **Application of seaFAST-pico system and SF-ICP-MS for determination of uranium concentration and its isotopic ratios in seawater -** Irena Wysocka, Emilia Vassileva

TP-37 **Development of analytical procedure for determination of lanthanides at ng.L-1 level in mineral waters -** Irena Wysocka, Anna Rogowska

TP-38 **Fast and high throughput digestion method for soil and sediment analysis using a modified graphite digestion system -** Dian Wen, Dong Yan, Glenn Woods

TP-39 **Calibration for space-resolved laser ablation ICP-MS of tree rings -** Adrian Wichser, Matthias Trottmann, Jorg Niederberger, Davide Bleiner

TP-40 **Silver nanoparticles in natural water bodies - is it only humans who are to blame ? -** Andreas Wimmer, Michael Schuster

TP-41 **Determination of 239Pu, 240Pu concentration and 240Pu/239Pu atom ratio in seawater using an isotope dilution sector field-inductively coupled plasma-mass spectrometry -** Masatoshi Yamada, Jian Zheng

TP-42 **Assessment of heavy metals in surficial marine sediments from the Lebanese coast (Eastern Mediterranean) -** Mariam Zayter, Celine Mahfouz, Milad Fakhri, Hugues Preud'homme

TP-43 **"Bulk and trace elements» in saline water produced from the Danish North Sea: The chemical analysis and the trends in the retrieved data -** Sofie Gottfredsen, Niels Schovsbo, Karen Feilberg

TP-44 **Rapid analysis of Rare Earth Elements in freshwater by ICP-MS with online preconcentration** Johanna Ziebel, Loic Martin, Christophe Hissler, Cedric Guignard

TP-45 **Screening of metals in surface and drinking waters using semi quantitative analysis ICP-MS -** Jeroen Noerens, Els Van Meenen

TP-46 **Bio-indication of traffic impact on forest ecosystems -** Jitka Hegrová, Oliver Steiner, Petr Anděl, Stefan Tanda, Walter Goessler, Vilma Jandová, Roman Ličbinsky

TP-47 **Evaluation of lead in drinking water in daycare centres -** Elham Zeinijahromi, John Younger, Theron White, Jessica Popadynetz, Lorinda Butlin, David W. Kinniburgh

TP-48 **Microwave-assisted acid digestion of cannabis product -** David Reishofer, Melanie Wolf

TP-49 **ICP OES and LIBS approaches for the analysis of nickeliferous minerals -** Elizabet Abad Peña, Edenir Rodrigues Pereira-Filho, Marco Aurelio Speranca, Felipe Manfroi Fortunato, Tiago Augusto Castelani, Margarita Edelia Villanueva Tagle, Maria Teresa Larrea Marin, Mario Simeón Pomares Alfonso

Nanomaterial analysis

TP-50 **Analytical issues for the characterization of nanomaterials in consumer products for regulatorypurposes -** Francois Auger, Guillaume Bucher, Mathieu Menta, Lucile Marigliano, Olivier F.X. Donard, Fabienne Seby

TP-51 **Determination of nanopowders using MIP-OES operating in a single particle mode -** Magdalena Bartosiak, Jacek Giersz, Krzysztof Jankowski

TP-52 **Analytical monitoring of biological synthesis of selenium nanoparticles using PCVG-MIP-OES and UV-Vis spectrophotometry and their further application as a mercury detoxifying agent -** Magdalena Bartosiak, Jacek Giersz, Krzysztof Jankowski

TP-53 **Automated solution for processing complex data sets generated in single particle and single cell analysis by ICP-TOF-MS -** Luca Flamigni, Olga Borovinskaya, Daniele Chiaretti, Oestlund Fredrik

TP-54 **Study of the ion cloud profiles from gold and silver nanoparticles in ICP-MS -** Joshua Fuchs, Maryam Aghaei, Harald Rosner, Tilo Schachel, Michael Sperling, Annemie Bogaerts, Uwe Karst

TP-55 **Contribution to SP-ICP-MS accurate spherical gold nanoparticles size determination: a comparison with small angle X-ray scattering -** Valerie Geertsen, Olivier Tache, Elodie Barruet, Frederic Gobeaux, Jean-Luc Lacour

TP-56 **Single particle ICP-MS as screening method for detection of nanoparticles -** Ana Gimenez-Ingalaturre, Celia Trujillo, Eduardo Bolea, Juan Castillo, Francisco Laborda

TP-57 **Optimization and application of single particle ICP-MS to TiO2 nanoparticles analysis in foodstuffs -** Lucas Givelet, Petru Jitaru, Delphine Boutry, Jean-Francois Damlencourt, Thierry Guerin

TP-58 **Synthesis and characterization of tellurium based nanoparticules through a multitechnique platform including hyphenated ICP-MS techniques -** Beatriz Gomez Gomez, Jon Sanz Landaluce, Teresa Perez Corona, Yolanda Madrid Albarran

TP-59 **Challenges and solutions for measuring small sized nanoparticles -** Chia-Chin(donna) Hsu, Ching-Heng(jones) Hsu, Yen-Ying(brian) Liao, Michiko Yamanaka, Yoshinori Shimamura, Glenn Woods, Chiu-Hun Su

TP-60 **Interaction of silver nanoparticules with agricultural soils: effects to size and chemical form -** Monica Iglesias, Laura Torrent, Eva Margui, Manuela Hidalgo

TP-61 **Size characterization and speciation of gold and silver nanoparticles and their ionic counterparts by hydrodynamic chromatography coupled to ICP-MS -** Maria Jimenez, Daniel Isabal, Maria Gomez, Francisco Laborda, Juan Castillo

TP-62 **The potential of single particle ICP-MS for the characterization of metallic nanoparticles in complex clinical and toxicological samples -** Maria Jimenez-Moreno, Sergio Fernandez-Trujillo, Angel Rios, Rosa Carmen Rodriguez Martin-Doimeadios

TP-63 **Different nanoparticles characterization: comparison of different sample introduction strategies using inductively coupled plasma mass spectrometry (ICPMS) -** Jovana Kocić, Detlef Günther, Bodo Hattendorf

TP-64 **New calibration approaches for Ag-NPs characterization in complex samples by SP-ICP-MS -** Diego Leite, Raquel Sanchez, Carlos Sanchez, José Luis Todoli, Maite Aramendia, Martin Resano

TP-65 **Evaluating TiO2 nanoparticles in sunscreens by single particle ICP-MS (SP-ICP-MS) -** Riccardo Magarini, Helmut Ernstberger, Enrico Sabbioni

TP-66 **Development of a novel analytical strategy for the identification and quantification of nanoplastics by ICPMS -** Lucile Marigliano, Javier Jimenez-Lamana, Stephanie Reynaud, Bruno Grassl, Elise Deniau, Joanna Szpunar

TP-67 **Asymmetrical flow field-flow fractionation hyphenated with ICP-MS for trace level analysis of engineered silver nanoparticles in river water -** Florian Meier, Robert Reed, Roland Drexel

TP-68 **Extracting nanoparticles: how is it done in SP-ICP-MS with microsecond time resolution, when continuous background is present? -** Darya Mozhayeva, Carsten Engelhard

TP-69 **Heteroatom incorporation during MFI crystallization as measured by single particle inductively coupled plasma mass spectrometry -**Jenny Nelson, Tracy Davis

TP-70 **Investigating the impact of nano-pesticides on plants, soil and waste water sludge using SP-ICP-MS -** Jenny Nelson, Arturo Keller, Yuxiong Huang

TP-71 **Analysis of chromium immobilization on zero-valent iron nanoparticles by ICP-OES -** Ivan Nemet, Sanda Rončević, Leontina Toth

TP-72 **Use of a mini-channel in AF4-ICP-MS for detection and characterization of titanium dioxide nanoparticles in consumer products -** David Ojeda, Eduardo Bolea, Francisco Laborda, Juan Castillo

TP-73 **AF4-ICP-MS as a powerful tool for the study of platinum nanoparticles in water samples -** Rosa Rodriguez Martin-Doimeadios, Armando Sanchez-Cachero, Nuria Rodriguez Farinas, Angel Rios

TP-74 **Simultaneous measurement of multiple isotopes and elements in nanoparticles using a multi-collector ICPMS with microsecond speed electronics and wide range Daly ion counters -** Phil Shaw, Takafumi Hirata, Mirai Ishida, Philip Freedman, Shuji Yamashita

TP-75 **Calculation considerations for characterizing silver nanoparticles with different properties in environmental samples by single particle inductively coupled plasma mass spectrometry -** Laura Torrent, Francisco Laborda, Monica Iglesias, Eva Margui, Manuela Hidalgo

TP-76 **Characterization of silver species released from clays coated with silver nanoparticles in in vitro gastrointestinal digestion using AF4-ICP-MS -** Celia Trujillo, Eduardo Bolea, Isabel Abad-Alvaro, Josefina Perez-Arantegui, Francisco Laborda, Juan Castillo

TP-77 **Detection of nanoparticles released from metallic food additives by single particle ICP-MS -** Celia Trujillo, Ana Gimenez-Ingalaturre, Josefina Perez-Arantegui, Francisco Laborda, Juan Castillo

TP-78 **New algorithms for enhancing particle detection in SP-ICP-MS -** Jani Tuoriniemi, Geert Cornelis

TP-79 **Nanoparticle analysis in semiconductor grade chemical reagents -** Michiko Yamanaka, Yoshinori Shimamura, Chia-Chin (donna) Hsu, Glenn Woods

TP-80 **Determination of substrate-assisted laser desorption ICP-MS transport efficiency of gold nanoparticles -** František Zelenák, Viktor Kanický, Jan Preisler

TP-81 **Analysis of nanoparticles in organic solvents using single particle ICP-MS with multi-spray CGrid nebulizer -** Koyo Ido, Shin-Ichi Miyashita, Yanbei Zhu, Tomoko Ariga, Shin-Ichiro Fujii, Akiko Hokura, Kazumi Inagaki

TP-82 **In vitro gold nanoparticles uptake into tumour cells: an analysis by SP-ICP-MS -** Johanna Noireaux, Romain Grall, Marie Hullo, Sylvie Chevillard, Emilie Brun, Caroline Oster, Katrin Loeschner, Paola Fisicaro

TP-83 **Analysis of titanium dioxide nanoparticles in biological fluids using single particle ICP-MS -** Samantha Salou, Ciprian Mihai Cirtiu

TP-84 **Overcoming spectral overlap in the characterization of iron nanoparticles by means of single-particle ICP-mass spectrometry (SP-ICP-MS): chemical versus physical resolution -** Ana Rua-Ibarz, Guillermo Pozo, Eduardo Bolea-Fernandez, Frank Vanhaecke, Xochitl Dominguez, Kristof Tirez

TP-85 **Comparison of SP-ICP-MS and SMPS: Different measurement principles for the determination of the size of nanomaterials -** Philipp Reichardt, Florian Steinberg, Frank Bierkandt, Jutta Tentschert, Sandra Wagener, Daniel Rosenkranz,2, Peter Laux, Andreas Luch

TP-86 **Nanoparticles biodistribution studies: Optimization of lung digestion protocols for TiO2 NPs analyses by SP-ICP-MS -** Ibtihel Ben-Dhiab

TP-87 **The role of single particle ICP-MS with microsecond time resolution in a multi-technique approach for unveiling the biological fate of ingested nanoparticles -** Federica Aureli, Francesca Ferraris, Sara Savini, Jessica Ponti, Dora Mehn, Andrea Raggi, Francesca Iacoponi, Douglas Gilliland, Luigi Calzolai, Francesco Cubadda

Posters – Wednesday, February 6th

Imaging and Bioimaging

WP-1 **Nano Secondary Ion Mass Spectrometry (NanoSIMS) for nanoparticle and trace element imaging in mammalian cells -** Maria Angels Subirana, Sarah Thomas, Felix Glahn, Gerd Hause, Sina Riemschneider, Martin Herzberg, Dirk Dobritzsch, Dirk Schaumlöffel

WP-2 **LA-ICP MS study of Ag nanoparticle transport in a 3-dimensional in vitro model -** Akihiro Arakawa, Norbert Jakubowski, Sabine Flemig, Heike Traub, Mate Rusz,Gunda Koellensperger, Daigo Iwahata, Takafumi Hirata

WP-3 **Complementary bioimaging by means of LA-ICP MS and MALDI-MS - Detection of adofluorine P in mouse heart tissue after myocardial infarction -** Rebecca Buchholz, Moritz Wildgruber, Uwe Karst

WP-4 **Gadolinium in human brain sections and co-localization with other elements after macrocyclic GBCA administration -** Ahmed El-Khatib, Helena Radbruch, Sabrina Trog, Boris Neumann, Friedmann Paul, Arend Koch, Michael Linscheid, Eyk Schellenberger, Norbert Jakubowski

WP-5 **Laser ablation ICP MS for simultaneous quantitative imaging of iron and ferroportin in hippocampus region of human brain tissues with Alzheimer's disease -** Beatriz Fernandez, Maria Cruz-Alonso, Susana Junceda, Aurora Astudillo, Ana Navarro, Rosario Pereiro

WP-6 **Bioconjugated gold nanoclusters as labels in quantitative imaging of metallothioneins in ocular tissues by LA-ICP MS -** Beatriz Fernandez, Maria Cruz-Alonzo, Montserrat Garcia, Hector Gonzalez-Iglesias, Rosario Pereiro

WP-7 **Isotopically-enriched tracers and ICP–MS methodologies to study zinc supplementation in singlecells of retinal pigment epithelium in vitro -** Beatriz Fernandez, Sara Rodriguez-Menendez, Hector Gonzalez-Iglesias, Montserrat Garcia, Lydia Alvarez, Jose Ignacio Garcia Alonso, Rosario Pereiro

WP-8 **Thulium spiked gel for internal standardisation in LA ICP MS bioimaging: quantitative elemental distribution of uranium in kidney tissue -** Nagore Grijalba, Alexandre Legrand, Yann Gueguen, Valerie Holler, Celine Bouvier-Capely

WP-9 **Application of laser ablation inductively coupled plasma mass spectrometry for investigation of Li, Mn, Co and Ni deposition patterns on carbonaceous anodes in lithium ion batteries -** Patrick Harte, Martin Winter,2, Sascha Nowak

WP-10 **LA-ICP MS as a tool for assessment of the accumulation of minerals and trace elements in the arterial wall samples with advanced atherosclerotic lesions -** Adam Sajnóg, Anetta Hanć, Bogna Gryszczyńska, Wacław Majewski, Maria Iskra, Danuta Barałkiewicz

WP-11 **Investigation of the delivery of platinum bisphosphonates to hard bone tissue using LA-ICP MS -** Lukas Schlatt, Barbara Crone, Robin Nadar, Sander Leeuwenburgh, Michael Sperling,3, Uwe Karst

WP-12 **Nanoparticles as tags for protein tissue analysis using laser ablation inductively coupled plasma and mass spectrometry -** Michaela Tvrdoňova, Roman Hrstka, Masařik Michal, Marcela Vlcnovska, Marketa Vaculovicova, Viktor Kanicky 5, Tomas Vaculovic

WP-13 **Imaging of specific proteins by LA-ICP MS -** Tomas Vaculovic, Michaela Tvrdonova, Marketa Vaculovicova, Marcela Vlcnovska, Viktor Kanický, Michal Masarik, Roman Hrstka, Hana Polanska

WP-14 **Bioimaging of proteins in human ocular tissue sections by LA-ICP MS using isotopically enriched silver nanoclusters as labels -** Eva Valencia, Maria Cruz-Alonzo, Beatriz Fernandez, Hector Gonzalez-Iglesias 5, Rosario Pereiro

WP-15 **Super resolution reconstruction for bioimaging by LA ICP MS -** Mika Westerhausen, David Bishop,2, Nerida Cole, Jonathan Wanagat, Philip Doble

WP-16 **Combination of high sensitivity and a fast full mass range scanning capability for imaging by laser ablation ICP MS: performance of the high resolution ICP MS AttoM ES -** Ariane Donard, Phil Shaw, Leon Eldridge

WP-17 **Investigation of galvanic anode metal uptake in individual marine organisms (Corophium volutator) via complementary ETV-ICP MS/LA-ICP MS -** Marcus Von Der Au, Hannah Karbach, Anna Maria Bell, Sebastian Buchinger, Bolle Bauer, Uwe Karst, Björn Meermann

WP-18 **Evaluation of ionization efficiency/sensitivity enchancement for a range of aerosol delivery systems for LA-ICP MS -** Martin Šala, Vid Simon Šelih, Johannes T. Van Elteren

WP-19 **Evaluation of the state-of-the-art LA-ICP MS systems for elemental imaging of decorative glass object -** Vid Simon Šelih, Martin Šala, Johannes T. Van Elteren, Thibaut Van Acker, Frank Vanhaecke

WP-20 **Image analysis for 2D LA-ICP MS bioimaging -** Stephan Wagner, Katharina Halbach, Till Luckenbach, Stefan Scholz, Thorsten Reemtsma

Laser Ablation Plasma Spectrochemistry

WP-21 **Of laser ablation and standards when analyzing hard biological materials -** Matthieu Baudelet, Mauro Martinez

WP-22 **Quantitative determination of Cu via LA-ICP MS in single triple negative breast tumor cells after treatment with a new Cu phosphine complex -** Legna Andreina Colina Vegas, Thibaut Van Acker, Wilmer Villarreal, Alzir Azeved Batista, Olivier De Wever, Joaquim Araujo Nobrega, Frank Vanhaecke

WP-23 **Data processing software for LA-ICP MS -** Veronika Dillingerova, Viktor Kanicky, Vaculovic Tomas

WP-24 **Assessment of ns-LA coupled to MC-ICP MS for Fe isotopic analysis of meteoritic materials -** Claudia Gonzalez De Vega, Marta Costas Rodriguez, Thibaut Van Acker, Steven Goderis, Frank Vanhaecke

WP-25 **Provenance determination of ancient Roman imperial coinage with tandem LA-ICP MS/LIBS -** Felix Horak, Jakob Willner, Manfred Schreiner,3, Andreas Limbeck

WP-26 **A LA-ICP MS quantification strategy for the determination of particle-bound Hg as collected in air monitoring filters -** Gonzalo Huelga-Suarez, David Douglas, Heidi Goenaga-Infante

WP-27 **Improving accuracy and precision in LA-MC-ICP MS -** Penelope Lancaster

WP-28 **Adaptation and improvement of an elemental mapping method for lithium ion battery electrodes via of laser ablation inductively coupled plasma mass spectrometry -** Sascha Nowak, Patrick Harte, Maximilian Mense, Timo Schwieters, Marco Evertz, Martin Winter

WP-29 **Solid-spiking piking matrix matched isotope dilution laser ablation ICP MS for simultaneous determination of cadmium and chromium in sediments -** Javier Teran-Baamonde, Alatzne Carlosena, Rosa Soto-Ferreiro, Jose Andrade-Garda, Soledad Muniategui-Lorenzo

WP-30 **Accurate measurement of uranium isotope ratios in solid samples by laser ablation multi-collector inductively coupled plasma mass spectrometry -** Zsolt Varga, Michael Krachler, Adrian Nicholl, Markus Ernstberger, Thierry Wiss, Maria Wallenius, Klaus Mayer

WP-31 **Preparation and characterization of polymer-based multi elemental reference materials** - Julia Bode, Julia Schubert, Sabrina Stein, Carla Vogt

WP-32 **High Performance Thin Layer Chromatography coupled with LA-ICP MS and LDI/MALDI-FTICRMS to study asphaltenes -** Remi Moulian, Sandra Mounicou, Carine Arnaudguilhem, Johann Lemaitre, Juan Sebastian Ramirez-Pradilla,5, Marie Hubert-Roux,, Caroline Barrere-Mangote, Carlos Afonso,, Brice Bouyssiere, Pierre Giusti

WP-33 **Imaging artifacts in elemental bioimaging via LA-ICPMS due to excessive fluence and poor tissue preservation** - Joke Belza, Thibaut Van Acker, Eduardo Bolea-Fernandez, Frank Vanhaecke

WP-34 **Energy density control for selective ablation of biological material from a glass substrate using a nanosecond 193 nm laser -** Thibaut Van Acker, Stijn Van Malderen, Joke Belza, Eduardo Bolea-Fernandez, Frank Vanhaecke

WP-35 **Calibration methods for spatial determination of Platinum-based chemotherapy agents in tumor samples using LA-ICP MS bioimaging -** Ana Mendez-Vicente, Alexandre Calon, Nerea Bordel, Jorge Pisonero

Laser-Induced Breakdown Spectroscopy

WP-36 **Depth profiling of UV-light degradation of modern art materials using LIBS -** Lukas Brunnbauer, Laura Pagnin, Manfred Schreiner, Andreas Limbeck

WP-37 **Investigation of polymer degradation under corrosive conditions using tandem LA-ICP MS/LIBS -** Lukas Brunnbauer, Maximilian Mayr, Silvia Larisegger, Michael Nelhiebel, Johann Lohninger, Andreas Limbeck

WP-38 **Laser-induced breakdown spectroscopy in analysis of building materials -** Aleš Hrdlička, Jitka Hegrova, Jan Novotny, David Prochazka, Karel Novotny, Viktor Kanický, Jozef Kaiser

WP-39 **Quantitative multielemental mapping of biological samples by laser-induced breakdown spectroscopy: a case study of pig tissues -** Patrick Janovszky, Albert Keri, Lukas Brunnbauer, Andreas Limbeck, Gabor Galbács

WP-40 **Composition and morphology analysis of bimetallic nanoparticules generated in a spark discharge plasma -** Albert Keri, Henrik Bali, Lajos Villy, Attila Kohut, Tibor Ajtai, Zsolt Geretovszky, Gabor Galbács

WP-41 **Real-time sample surface height control and intensity normalization for laser-induced breakdown spectroscopy analysis of edible salts -** Yonghoon Lee, Hyang Kim, Sang-Ho Nam, Kyung-Sik Ham

WP-42 **Optimization and detailed spectroscopic characterization of an improved spatial heterodyne laser-induced breakdown spectroscopy setup -** David Palasti, Miklos Veres, Istvan Rigo, Zsolt Geretovszky, Eva Kovacs-Szeles, Ardian Gojani, Igor Gornushkin, Gabor Galbacs

WP-43 **Experimental optimization and assessment of the performance of laser-induced breakdown spectroscopy for the quantitative analysis of 20+ trace elements in uranium dioxide -** David Jenő Palasti, Adam Belteki, Eva Kovacs-Szeles, Andrey Berlizov, Gabor Galbacs

WP-44 **Shaping LIBS into a suitable tool for direct characterization of single nanoparticles: a brave new world -** Pablo Purohit, J. Javier Laserna

WP-45 **Advanced analysis of Li7La3Zr2O12 (LLZO) using LIBS: determination of the H-content -** Stefan Smetaczek, Veronika Zeller, Daniel Rettenwander, Jurgen Fleig, Andreas Limbeck

Biological and Clinical Analysis

WP-46 **A systematic comparison between millisecond and microsecond dwell time SP-ICP MS for the selective discrimination of silver nanoparticles from ionic silver as required for biomedical applications -** Isabel Abad-Alvaro, Beatriz Gomez-Gomez, Dorota Bartczak, Susana Cuello-Nunez, Yolanda Madrid, Heidi Goenaga-Infante

WP-47 **Quantification of protein modifications using a multielemental ICP MS/MS generic strategy -** Francisco Calderon Celis, Jorge Ruiz Encinar

WP-48 **Quantification of cancer biomarkers in single cells using metal-tagged antibodies and SC-ICP MS -** Mario Corte-Rodriguez, Javier Alonso-Garcia, Maria Montes-Bayon, Norbert Jakubowski, Ulrich Panne

WP-49 **A higher order method for the determination of total phosphorus in human serum -** Fransiska Dewi, Wesley Zongrong Yu, Benny M. K. Tong, Ho Wah Leung, Richard Y. C. Shin, Tang Lin Teo, Tong Kooi Lee

WP-50 **Conventional immuno-PCR in combination with inductively coupled plasma mass spectrometry for the determination of proteins: human epidermal growth factor receptor 2 (HER2) -** Alejandro Fernandez Asensio, Luisa Maria Sierra Zapico, Elisa Blanco Gonzalez, Maria Montes-Bayon

WP-51 **Analysis of chromium and other trace elements in whole blood -** Martin Gleisner

WP-52 **IDMS based quantification methods for metalloproteins as potential biomarkers for Alzheimer's disease -** Julia Gleitzmann, Sabrina Peters, Christine Brauckmann, Claudia Swart

WP-53 **Mass spectrometry imaging in clinical pathology: MMP-11 as a breast cancer biomarker -** Raquel Gonzalez De Vega, David Clases, Maria Luisa Fernandez-Sanchez, Noemi Eiro, Luis Gonzalez, Francisco Vizoso, Uwe Karst, Alfredo Sanz-Medel, Philip Doble

WP-54 **High resolution imaging of explant cultures to predict cisplatin resistance in anticancer therapy -** Calum Greenhalgh, Ellie Karekla, J. Howard Pringle, Amy Managh

WP-55 **Analysis of trace impurities in sunflower oil by HR-ICP OES –** Peio Riss, Margrit Killenberg, Sebastian Wunscher, Jan Scholz

WP-56 **Multi-element determination in populations of single cells by ICP MS** - Tetsuo Kubota, Michiko Yamanaka, Glenn Woods

WP-57 **New strategy for sensitive detection of circulating tumoral cells (CTCs) for breast cancer diagnostic -** Andrea Larraga, Noemi Eiro, Francisco J. Vizoso, Maria Luisa Fernandez-Sanchez

WP-58 **Optimization of protein quantification via isotope dilution ICP MS of a standard reference protein -** Nora Lemke, Ahmed El-Khatib, Franz Theuring, Jochen Vogl, Norbert Jakubowski

WP-59 **Platinum nanoclusters as metal labels to determine specific proteins in biological samples by bimodal detection (LA-ICP MS and fluorescence) -** Ana Lores Padin, Maria Cruz-Alonso, Hector Gonzalez-Iglesias, Beatriz Fernandez, Rosario Pereiro

WP-60 **Modified method of single cell analysis by quadrupole ICP MS -** Judy Lum, Kelvin Leung

WP-61 **Investigating hereditary hemochromatosis by means of LA-ICP MS/MS -** Jennifer-Christin Muller, Lisa Trager, Andrea Steinbicker, Michael Sperling, Uwe Karst

WP-62 **Advances in triple quadrupole ICP MS for clinical research analysis -** Simon Nelms, Chris Harrington, Geoff Carpenter, Jonathan Dart, Craig Mills, Daniel Kutscher

WP-63 **An integrated LC-ICP MS and LC-ESI-MS approach for the characterization of purified selenoprotein P -** Laurent Ouerdane, Jérémy Lamarche, Luisa Ronga, Katarzyna Bierla, Joanna Szpunar, Ryszard Łobiński

WP-64 **Direct analysis of trace elements in beer and wort by ICP OES -** Michael Petrich, Olaf Paulsen, Tuur Mertens, Daniela Grothusheitkamp, Thomas Kunz, Erica Cahoon

WP-65 **Challenges in bio-monitoring – total and single particle analysis -** Ewa Pruszkowski

WP-66 **Size exclusion chromatography ICP MS for trace level detection of gadolinium species accumulated in rat brain one month after single intravenous injection with gadolinium contrast agents -** Izabela Strzemińska, Cecile Factor, Philippe Robert, Joanna Szpunar, Ryszard Łobiński

WP-67 **Study of the use of biocompatible nanostructures to improve cisplatin performance in cell models: ferritin as nanocage -** Daniel Turiel-Fernandez, Jorg Bettmer, Elisa Blanco, Maria Montes-Bayon

WP-68 **A microwave-digestion approach for determination of osmium in chemical drug to meet the requirement of USP< 232>/< 233> -** Xiangcheng Zeng, Kazuhiro Sakai, Glenn Woods

WP-69 **Arsenic speciation in human urine after ingestion of husked rice -** Tatiana Pedron, Bruno Batista, Fernanda Paniz, Bruna Freire, Gustavo Barcelos

WP-70 **Leaching experiment followed by trace element analysis in fermentation media -** Katja Montan, Oliver Popp, Michael Molhoj

WP-71 **Mercury determination in dried blood spots -** Martin Resano, Raul Garde, Flavio Nakadi, Marcia Da Veiga, Julio Cruces

WP-72 **A feasible approach for determining bromine and iodine in human hair using interference-free plasma based technique -** Diogo Novo, Rodrigo Pereira, Alessandra Henn, Vanize Costa, Erico Flores, Marcia Mesko

WP-73 **Ultra trace U/Th dating of archaeological biominerals applying fsLA-HR-ICPMS -** Asmodée Galy, Loïc Martin, Fanny Claverie, Gaëlle Barbotin, Edwige Pons-Branchu, Nicholas J. Conard, Guillaume Porraz, Aurore Val, Chantal Tribolo, Norbert Mercier, Christophe Pécheyran

Posters - Thursday, February 7th

Stable Isotope Analysis

THP-1 **Provenancing of fish via elemental and strontium isotopic analysis of hard and soft tissues by (MC-) ICP MS -** Melanie Diesner, Andreas Zitek, Christine Opper, Maximilian Wrede, Anastassiya Tchaikovsky, Stephan Hann, Thomas Prohaska

THP-2 **Determination of lead isotope ratios in Antarctic snow by quadrupole ICP-DRC-MS using a total-consumption sample introduction system -** Francisco Ardini, Andrea Bazzano, Frank Vanhaecke, David Cappelletti, Marco Grotti

THP-3 **Isotopic and multi-elemental signatures as indicators of origin of sparkling wines -** Robin Cellier, Sylvain Berail, Julien Barre, Ekaterina Epova, Olivier Donard

THP-4 **Tracing the geographical origin of food products with multielement fingerprinting, isotope ratios and chemometrics: the case of Rocha pear -** Ines Coelho, Ana Matos, Ana Nascimento, Joao Bordado, Olivier F.X. Donard, Ekaterina Epova, Sylvain Berail, Isabel Castanheira

THP-5 **Microsampling approaches for isotopic analysis: focus on Wilson's disease patients -** Mcarmen Garcia Poyo, Maite Aramendia, Martin Resano, Sylvain Berail, Christophe Pecheyran

THP-6 **Factors determining limits of detection -** Martin Gleisner

THP-7 **Serum magnesium isotopic signature in type I diabetes -** Rosa Grigoryan, Marta Costas-Rodriguez, Steven Van Laecke, Marijn Speeckaert, Frank Vanhaecke

THP-8 **Strontium isotope ratio used as provenance indicator for milk samples from different regions in Slovenia -** Staša Hamzić Gregorčič, Tea Zuliani,2, Nives Ogrinc

THP-9 **Comparison of four mass spectrometric techniques for lithium isotopic measurements -** Hélène Isnard, Michel Aubert, Gwendoline Buzance, Laurence Longuet, Mylene Marie, Anthony Nonell, Fabien Pilon, Michel Tabarant, Karine Vielle

THP-10 **Bringing white into light: a multi-analytical approach studying lead-white pigments in paintings -** Stefan Kradolfer, Laura Hendriks, Irka Hajdas, Bodo Hattendorf, Hans-Arno Synal, Detlef Günther

THP-11 **Elemental and isotopic analysis of serum from agerelated macular degeneration patients by means of single-collector and multi-collector sector field ICP - mass spectrometry -** Lara Lobo, Marta Aranaz, Marta Costas-Rodriguez, Rosario Pereiro, Frank Vanhaecke

THP-12 **Direct determination of isotopic ratio of chromium species by HPLC–low resolution multicollector ICP MS -** Cuc Thi Nguyen-Marcińczyk, Jakub Karasiński, Marcin Wojciechowski, Ewa Bulska, Ludwik Halicz

THP-13 **Sr and Pb isotope ratio analyses and its application to investigate cultural interactions in ancient Nubia (2nd millennium BC) -** Anika Retzmann, Tristan Zimmermann, Johanna Irrgeher, Daniel Profrock, Julia Budka, Thomas Prohaska

THP-14 **Trace of anthropogenic nitrate in groundwater by isotopic proxies in Kumamoto area, Japan -** Naoto Sugimoto, Masasuke Sakiyama, Takahiro Hosono, Masaharu Tanimizu

THP-15 **Calibration of Mg isotope amount ratios and delta values -** Jochen Vogl, Olaf Rienitz, Bjorn Brandt, Simone Kasemann, Rebecca Kraft, Dmitry Malinovsky, Anette Meixner, Janine Noordmann, Savelas Rabb, Jan Schuessler, Robert Vocke, Martin Rosner

THP-16 **Stable isotope ratio analysis of Pb, S and Sr in plant available element fractions: targeted sampling and onsite interferent separation by diffusive gradients in thin films (DGT) -** Stefan Wagner, Ondrej Hanousek, Jakob Santner, Markus Puschenreiter, Walter Wenzel, Thomas Prohaska

THP-17 **Submicrogram sulfur isotope analysis by EA-MC-ICPMS -** Aaron Wilkins, Thomas Prohaska, Kerri Miller, Johanna Irrgeher, Michael Wieser

THP-18 **Hg isotopic measurements for atmospheric mercury at the Cape Hedo atmosphere and aerosol monitoring station (CHAAMS), Japan -** Akane Yamakawa, Akinori Takami, Yuji Takeda, Yoshizumi Kajii, Shungo Kato

THP-19 **Analysis of anthropogenic Gd emissions into the German North Sea and potential new insights by the analysis of Gd isotope ratios in MRI contrast agents -** Tristan Zimmermann, Ole Klein, Tobias Orth, Bettina Oppermann, Anika Retzmann, Johanna Irrgeher, Daniel Profrock

THP-20 **On-line coupling of a liquid chromatograph to a multicollector ICP MS for the direct measurement of Pb isotope ratios in samples of archaeological interest -** Pelayo Alvarez Penanes, Mariella Moldovan, J. Ignacio Garcia Alonso

THP-21 **Past environmental pollution in an industrial site: using stable lead isotopic analysis to identify multiple contamination sources -** Loris Calgaro, Alessandro Bonetto, Elena Badetti, Antonio Marcomini

THP-22 **Determination of $^{236}U/^{238}U$ ratios in environmental samples using ICP MS/MS -** Silvia Diez-Fernandez, Carole Bresson, Frederic Chartier, Olivier Evrard, Amelie Hubert, Hugo Jaegler, Anthony Nonell, Fabien Pointurier, Hélène Isnard

THP-23 **Submicrogram sulfur isotope analysis by EA-MC-ICP MS -** Aaron Wilkins, Thomas Prohaska, Kerri Miller, Johanna Irrgeher, Michael Wieser

THP-24 **Comparison of different mass bias correction procedures for the measurement of Hg species-specific isotope ratios by gas chromatography coupled to multicollector ICP MS -** Laura Suarez Criado, Jose Ignacio Garcia Alonso, Silvia Queipo Abad, Pablo Rodriguez Gonzalez

THP-25 **IUPAC Commission on Isotopic Abundances and Atomic Weights –** CIAAW - Johanna Irrgeher, Thomas Prohaska, Juris Meija

Elemental Speciation and Metallomics

THP-26 **Combining speciation analysis, multielement fingerprints and multivariate statistics to identify mussel farming sites affected by environmental inorganic arsenic of volcanic origin -** Federica Aureli, Mauro Esposito, Andrea Raggi, Francesca Iacoponi, Giuseppe Picazio, Teresa Bruno, Francesca Ferraris, Sara Savini, Francesco Cubadda

THP-27 **"Not your kid's apple juice»: an examination of arsenic content in american and european hard ciders -** Patricia Atkins, Elaine Hasty

THP-28 **Trace elements bioaccumulation and As biotransformation in sponges: uses of ICP MS methodologies -** Aurelie Barats, Anna Maria Orani, Eva Ternon, Olivier Thomas

THP-29 **The fascinating world of arsenic speciation in mushrooms -** Simone Braeuer, Jan Borovička, Walter Goessler

THP-30 **The use of ICP MS for the characterization of selenocompounds in bio-stimulated selected tomato varieties -** Ewa Bulska, Eliza Kurek, Magdalena Michalska-Kacymirow, Olga Kościuczuk, Anna Tomiak

THP-31 **Hyphenated techniques for the characterisation and application of metal labelled antibodies -** David Clases, Raquel Gonzalez De Vega, Philip Doble

THP-32 **Provision of calibration services to underpine selenium speciation measurements in the clinic: results from a phase I trial of selenium in cancer patients -** Maria Estela Del Castillo Busto, Christian Ward-Deitrich, Michael Jameson, Heidi Goenaga-Infante

THP-33 **Towards high throughput in speciation monitoring -** Helmut Ernstberger, Eve Kroukamp, Simone Korstian

THP-34 **Identification of cobalamin analogues in canine and equine urine via LC-MS-MS -** George Ganio, Paul Zahra, Katherine Ganio

THP-35 **Experimental and analytical approaches to elucidate the role of phytoplankton in biotic and abiotic mercury (Hg) transformation -** Javier Garcia-Calleja, Thibaut Cossart, Zoyne Pedrero, Laurent Ouerdane, Emmanuel Tessier, Vera Slaveykova, David Amouroux

THP-36 **Ultratrace analysis of germanium species in natural waters by cryotrapping with ICP MS and ICP MS/MS detection -** Adrian Garcia-Figueroa, Montserrat Filella, Tomaš Matoušek

THP-37 **Investigation of transition metal species in lithium ion battery electrolytes by means of CE-ICP MS – a new approach to reveal the dissolution mechanism of transition metals from cathode materials -** Lenard Hanf, Martin Winter, Sascha Nowak

THP-38 **Studies on the influence of metal ions on maize (Zea mays) using LA-ICP MS and ESI-MS/MS -** Anetta Hanć, Arleta Małecka, Piotr Kachlicki, Adam Sajnog, Wiktor Lorenc, Danuta Barałkiewicz

THP-39 **Determination of the geographic origin of spices using elemental analysis after microwave digestion -** Elaine Hasty, Tina Restivo, Jenny Nelson, Courtney Tanabe, Greg Gilleland, Lindsey Whitecotton

THP-40 **Maternal dietary habits, levels of selected elements and fatty acids composition in human milk from coastal and inland areas of Slovenia -** Marta Jagodic, Janja Snoj Tratnik,, Doris Potočnik, Darja Mazej, Tome Eftimov, Nives Ogrinc, Milena Horvat

THP-41 **Tools for elemental speciation in clay - from CE-ICP MS speciation to miniaturised clay column experiments using LC-ICP MS -** Ralf Kautenburger, Kristina Brix, Christina Hein, Jonas Sander, Guido Kickelbick

THP-42 **Boron isotope - amount ratio analysis via MC-ICP MS in seawater and freshwater samples after microsublimation -** Ole Klein, Tristan Zimmermann, Johanna Irrgeher, Daniel Pröfrock

THP-43 **Development of a LC-ICP MS with a counter gradient method for quantification of decomposition products of lithium ion battery electrolytes -** Kristina Koesters, Jonas Henschel, Martin Winter, Sascha Nowak

THP-44 **Validated procedures of isotope dilution ICP MS coupled with HPLC for determination of selenium species in food samples -** Agnieszka Krata, Marcin Wojciechowski, Jakub Karasiński, Eliza Kurek, Ewa Bulska

THP-45 **Natural and ^{82}Se-labelled selenomethionine certified reference materials -** Kelly Leblanc, Phuong Mai Le, Jianfu Ding, Zoltan Mester

THP-46 **Speciation of arsenic in alcoholic beverages using LC ICP MS/MS -** Jolette Macaulay, Connie Samson, Carolyn Barry, Cory Murphy, Beata Kolakowski

THP-47 **An investigation on the influence of the chemical forms of arsenic for the accurate determination of total arsenic in rice -** Sang Ho Nam, Won Bae Lee, Yonghoon Lee

THP-48 **Snapshots of metal speciation via liquid chromatography inductively coupled plasma mass spectrometry -** Heather Neu, Kiwon Ok, Sergei Alexishin, James Polli, Maureen Kane, Sarah Michel

THP-49 **Feasibility study for the determination of arsenic species in nutritional products and raw ingredients by HPLC ICP MS -** Lawrence Pacquette, Jenny Nelson, Courtney Tanabe

THP-50 **Simultaneous iodine and bromine speciation analysis in infant formula using HPLC-ICP MS** - Lawrence Pacquette, Jenny Nelson

THP-51 **Application of ICP MS technique for investigation of new possibilities in extraction of trace metals using NADES -** Lena Ruzik, Natalia Osowska

THP-52 **Development and validation of a method for ultra-trace - speciation analysis of chromium in foodstuff by HPLC ICP MS using species specific isotope dilution -** Marina Saraiva

THP-53 **Quantitative LA-ICP-TOF-MS bioimaging** - Andreas Schweikert, Sarah Theiner, Anna Schoeberl, Sophie Neumayer, Bernhard K. Keppler, Gunda Koellensperger

THP-54 **Complexation strategy for SEC-ICP MS for the analysis of protein adducts with ethylmercury from thiomersal in influenza vaccines** - Philipp Strohmidel, Michael Sperling, Uwe Karst

THP-55 **Elemental analysis of the changes in the metal profiles and arsenic species during wine processing** - Courtney Tanabe, Jenny Nelson, Susan Ebeler

THP-56 **Multi-elemental (As, Sn and Hg) speciation in wines by HPLC- or GC-ICP MS -** Véronique Vacchina, Ekaterina Epova, Sylvain Berail, Olivier Donard, Fabienne Seby

THP-57 **Lead in wine : total concentrations, speciation and isotopic signatures** - Véronique Vacchina, Ekaterina Epova, Fanny Claverie, Sylvain Berail, Christophe Pecheyran, Fabienne Seby, Olivier Donard

THP-58 **Evaluation of a complete workflow for the determination of arsenic species in fish and rice** - Wolfram Weisheit, Rene Chemnitzer, Katharina Vlach, Philipp-Frederic Schulz

THP-59 **Development of SEC–ICP MS/MS method to evaluate the formation of DNA-protein complexes -** Ines Zarfaoui, Frederique Bessueille-Barbier, Agnes Hagege, Linda Ayouni-Derouiche

THP-60 **Comprehensive speciation analysis of metal complexes in coconut water as a model for method development for studies of plant endosperm metallome** - Ghaya Alchoubassi, Katarzyna Kinska, Katarzyna Bierla, Joanna Szpunar

THP-61 **Simultaneous analysis of selenium and arsenic in drinking water with LC-ICP MS** - Xu Junjun, Lu Qiu-Yan, Glenn Woods

THP-62 **The formation of plant-based antimony nanoparticles by inorganic Sb species** - Bill Maher, Tona Sanchez-Palacios, Christopher Johnston, Simon Foster

THP-63 **Exploring the generation of volatile mercury species by cryotrapping with ICP MS detection** - Radek Židek, Lucie Juhaszova, Inga Petry-Podgorska, Jan Kratzer, Tomaš Matoušek

THP-64 **Determination of selenoproteins in human serum from lung cancer patients by IDA-SEC-AP-ICP-QQQ-MS -** Belen Callejon-Leblic, Jose Luis Gomez-Ariza, Antonio Pereira Vega, Tamara Garcia-Barrera

THP-65 **Metals traffic and metabolomic alterations caused by the antagonistic interaction of cadmium and selenium using organic and inorganic mass spectrometry -** Gema Rodriguez Moro, Rocio Baya Arenas, Jose Luis Gomez-Ariza, Francisco Navarro Roldan, Tamara Garcia-Barrera

THP-66 **Investigation of arsenolipids in brain and muscle tissues of skipjack tuna using HPLC-mass spectrometry -** Michael Stiboller, Fabiana P. Freitas, Tanja Schwerdtle, Kevin A. Francesconi, Georg Raber

THP-67 **Comparison of two sensitive methods for the - quantification of Cr (VI) in surface and drinking waters with IC-ICP MS and LC-ICP QQQ -** Els Van Meenen, Jeroen Noerens

THP-68 **Quantitative speciation analysis for the in vivo study of iron metabolism and bioavailability from formula milk fortified with isotopically stable enriched iron oxohydroxide nanoparticles -** Rafaella Regina Peixoto, Sonia Fernandez-Menendez, Belen Fernandez-Colomer, Alfredo Sanz-Medel, Solange Cadore, Maria Luisa Fernandez-Sanchez

THP-69 **LA-ICP MS in brain imaging -** Olga Minaeva, Ning Hua, Nicola Lupoli, Erich Franz, Xiuping Liu, Sarah Rind, Katherine Babcock, Juliet Moncaster, Lee Goldstein

Advanced Materials and Industrial analysis

THP-70 **Rapid determination of lithium ion battery materials using ICP OES** - Wenkun Feng, Jeannie Ni, Glenn Woods

THP-71 **Analysis of complex metal oxide thin films by online-LASIL with ICP MS detection -** Christopher Herzig, Johannes Frank, Maximilian Morgenbesser, Alexander K. Opitz, Jurgen Fleig, Andreas Limbeck

THP-72 **Determination of Ba, Cs, Mo, Zr and U in SIM Fuel samples by ICP OES and ICP MS for the study of fission products behavior during a nuclear severe accident -** Alexandre Labet, Matthieu Aubert, Serge Pontremoli, Christophe Winkelmann, Claire Le Gall

THP-73 **Metallurgical analysis with Avio 500 ICP OES: dealing with matrices and interferences -** Benoit Martelat, Kenneth Neubauer, Wim Van Bussel, Aaron Hineman, Erica Cahoon

THP-74 **The evaluation of aluminium magnesium hydrotacite concentrations in Ziegler-Natta polymerized polyolefins for the prediction of discolouring processes -** Franky Puype

THP-75 **Validation of limits of quantitation in seawaters and brines by HR ICP OES -** Peio Riss

THP-76 **Determination of trace elements in line-rich matrices using HR-Array ICP OES –** Peio Riss, Sandro Spille, Margrit Killenberg, Sebastian Wunscher

THP-77 **Laser ablation chemical mapping of high efficiency Kesterite solar cells with lithium alloying -** Matthias Trottmann, Adrian Wichser, Davide Bleiner

THP-78 **High precision with ICP OES - What is possible in real examples and in routine? -** Dirk Wuestkamp, Oliver Primm

THP-79 **Ultra trace analysis in high purity materials by ICP OES -** Dirk Wuestkamp, Oliver Primm, Nicole Grabiger

THP-80 **Multiscale elemental analysis of buried materials and interfaces -** Patrick Chapon, Sofia Gaiaschi, Jocelyne Marciano

THP-81 **Direct solid sampling process accompanying analysis with ETV-ICP OES - Monitoring the feedstock quality of coal conversion processes -** Thomas Vogt, Daniela Vogt, Carla Vogt

Petroleum and Semiconductor Materials

THP-82 **Variable volatility of organic analyte forms in direct analysis, using ICP OES, HR-CS FAAS and HR-CS MAS - drawback or benefit? -** Zofia Kowalewska, Karolina Brzezińska

THP-83 **Towards a greener approach for microwave assisted acid digestion of refractory petroleum crude samples using a single reaction chamber system followed by ICP techniques -** Francisco Antonio Lopez-Linares, Fe Aguilar, Jorge Hernandez, Laura Poirier

THP-84 **Determination of chlorides in crude oils by direct dilution using ICP MS/MS -** Jenny Nelson, Laura Poirier, Francisco Lopez-Linares

THP-85 **In-service oil analysis with ICP OES following ASTM D5185 -** Kenneth Neubauer, Erica Cahoon, Chady Stephan, Autumn Wassmuth

THP-86 **Ethanol direct analysis of phosphorus, sulfur, copper and iron with the Avio 500 ICP OES –** Wim Van Bussel, Huynh Suong, Kenneth Neubauer, Erica Cahoon

Abstracts

Analytical chemistry: out of the box

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Analytical chemistry is the discipline in chemistry that scrutinizes the details of composition and structure of natural and man-made objects. To do that, it borrows from technological developments and scientific knowledge – from within chemistry itself, but also from other scientific disciplines such as *e.g.* physics and biology - to perform its basic tasks, solving particular scientific or technological problems. As a result of explosive developments in science and technology over the last few decades, the nature of analytical chemistry changed considerably, and evolved away from methods involving simple measurement processes. At present, it needs to address issues of growing complexity that require high sensitivity and selectivity together with increasing needs for fast repetitive measurements of a widening range of elemental and increasingly complex, often labile molecular species and structural arrangements. Despite the successes of analytical chemistry in the complex world of today, and maybe just because of its recent spectacular success stories, there still circulate distorted, often incomplete and minimalistic views on the essential features of the discipline and on its etymology. Therefore, it is not clear how it should be defined and related to other sciences, particularly to chemistry and metrology. In this lecture, I will briefly discuss some of the existing preconceptions and misinterpretations and tackle them from a different perspective, thus alleviating their effect while enlarging the scope of the discipline to its prevalent position in present-day science and technology.

Keywords: analytical chemistry, chemical analysis

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PLM-1 Past and recent developments in glow discharge optical emission spectroscopy (GD-OES)

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The first commercial Glow Discharge (GD) instrument for elemental analysis was the RSV Optical Emission Spectrometer (OES) introduced in 1968. Equipped with a Grimm type GD lamp, this basic design prevails to this day in GD-OES instrumentation. The design and characteristics of the Grimm source are briefly discussed, including analytical figures of merit. A comparison withthe "classical" spark and also the more recent LIBS techniques will be given. The development of Compositional Depth Profiling (CDP) with GD-OES is presented, with emphasis on quantitative CDP. Recent trends, both of instrumentation and data treatment methods, are presented. In particular, the impact of solid state detectors providing wide range spectral coverage is discussed, with emphasis on data treatment in the future. The novel Solution Cathode Glow Discharge (SCGD) sources will also be described with examples of analytical results. Another very exciting recent development is hyperspectral imaging using very large GD sources; some of the recent development and results will be presented.

Keywords: glow discharge, optical emission, elemental analysis, depth profiling, depth profile analysis, data treatment

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KM-1 Light element analysis by analytical glow discharges

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Analytical glow discharges with optical (GD-OES) and mass spectrometric (GD-MS) detections are able to obtain depth resolved information about the light elements hydrogen, carbon, nitrogen and oxygen in solid samples, where most of the other analytical techniques fail. Because the light element concentration and distribution mainly determine mechanical, optical or electromagnetic properties of many materials, a lot of essential analytical applications of GD exist.

However, the interpretation or even quantification of the measured signals sometimes is very challenging. Problems arise due to physical effects (plasma processes such as the 'Hydrogen effect', the Doppler effect, self absorption or diffusion of hydrogen in the sample during sputtering) chemical effects (e.g. formation of compounds with argon or the matrix, poisoning of the sample or gettering) as well as instrumental difficulties (*e.g.* of the sensitivity, calibration and vacuum quality).

The GD techniques are direct solid sampling methods and require reference materials for calibration. Unfortunately, the list of available certified reference materials (CRMs) suited for calibration of light elements in different matrix is relatively short. Therefore, sintered materials doped with the analytes H, O and N were produced at IFW Dresden and applied as calibration standards for hydrogen, oxygen and nitrogen. Due to the high analyte concentration added, it is very likely that the real concentrations agree well with the added amount of light elements in the corresponding phases. The validation of the determination of the light element concentration in the sintered samples was possible in some cases only due to the lack of suitable techniques. This fact proves the need for the development of a reliable matrix independent quantification of light elements by GDS.

The sintered calibration material was also used for fundamental investigations. Here, first time a systematic dependence of the sputtering rate (SR) on the concentration of the phases in phase mixtures was found and could be deduced from basic physical principles **[1]**.

Using sintered mixtures of TiH_2 and ZrH_2 with Cu, it was found that the ratio method **[2]** (e.g. I(H656)/I(Cu219)=f[c(H)/c(Cu)]) results in reproducible Cu matrix dependent calibration up to 1.5 m% H. Up to 0.25 m% H the dependence is linear. However, matrix independent calibration of H using the model of constant Emission Yields EY I(H)=c(H)*SR*EY does not work in GD-OES. This behaviour can be explained by a very similar quenching of the hydrogen and copper intensity caused by the "Hydrogen effect". A correction for this effect for real matrix independent H calibration in GD-OES will be discussed. First experiments with GD-MS show a linear dependence I(H)=f[c(H)*SR] up to 1.5 m% H and thus confirm the quenching of the EY in GD-OES.

Fundamental investigations have been also made about the influence of oxygen in analytical glow discharges **[3]** and the effect of Ar-O_2 mixtures compared with that of oxygen released from the sample **[4]**. This comparison proved that oxygen in a concentration, which is generated by sputtering of an oxide, has no major effect on the emission of spectra in GD-OES. Using sintered samples of Al_2O_3, CuO, Cu_2O and MgO mixed with Cu, Al and Mg, the blue line shift effect at O I 130.22 nm, first time reported by Köster 2009, was confirmed. The effect is more pronounced at Mg than in Al and Cu, which due to line interference leads to a matrix dependent EY at this wavelength. It will be shown that the effect is negligible at O I 777.19 nm and this EY is matrix independent. However, measurements in this NIR region require special spectrometer configuration and detection. GD-MS also produced promising results for the calibration of oxygen with these sintered samples, when the sputtering rate was included in the evaluation **[5]** and the discharge conditions are optimized.

More recently also sintered material for nitrogen calibration (AlN mixed with Al and Si_3N_4 mixed with Cu) was produced and points to a matrix independent EY of N I 174.27 nm.

Keywords: glow discharge spectrometry, light elements, hydrogen, oxygen, nitrogen, calibration

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KM-2 Current pros and cons of GD-MS and LA-ICP- MS for high spatially resolved elemental analysis

Jorge Pisonero [αβ 1], Jonatan Fandiño [1], Cristina Gonzalez-Gago, Alfredo Sanz-Medel [1], Silke Richter , Norbert Jakubowski [2], Nerea Bordel [1]

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Elemental analysis of solid samples with high spatial resolution (including in-depth and lateral resolution) and high sensitivity is greatly demanded in different research fields, such as material science, geology or biochemistry. In this context, pulsed glow discharge mass spectrometry (pulsed-GD-MS) is able to provide bulk and depth profile analysis with high sensitivity and excellent depth resolution, allowing the determination of ultra-traces in pure materials or the analysis of nano/micro-coatings. Complementarily, LA-ICP-MS has evolved to fast imaging capabilities with high sensitivity and high lateral resolution (mscale), allowing the determination of the distribution of minor/trace elements in geological and biological samples (e.g. distribution of nanoparticles or quantum dots in single cells). Nevertheless, there are still multiple drawbacks that need to be overcome in relation to quantification methods, operating conditions and so on. In this work, advantages and current limitations of both methods are discussed in detail making use of some representative examples related to different research fields.

Keywords: direct solid analysis, GD-MS, LA-ICP-MS, depth profile analysis, elemental imaging

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KM-3 Development of high-power pulsed microplasma emission source for ultrasmall sample analysis

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Trace elemental analysis of ultrasmall samples is required in many fields such as regenerative medicine and environmental sciences. Argon inductively coupled plasma (Ar-ICP) has widely served as an excellent excitation and ionization source in inorganic trace elemental analysis because it facilitates multielemental analysis with high-sensitivity. However, ICPs are too large and consumes disproportionately large amounts of power and gas for ultrasmall sample analysis. In recent years, microplasma, which exhibits a micrometer- scale characteristic length, has attracted remarkable attention from many research fields. In our research group, high-power pulsed microplasma (HPPM)[1], was developed and utilized as an excitation source for ultrasmall sample analysis. HPPM can realize a maximum power density of 5×10^8 W/cm3. The measured electron number density and excitation temperature were 3.7×10^{15} cm-3 and 7000 K at maximum, which demonstrated that the HPPM is a high-energy and high-density plasma source. However, power consumption is very small about 0.6 W for 1-Hz plasma generation, so the power supply could be downsized to produce a hand-held battery-driven device. In this lecture, some research topics of the application of HPPM for ultrasmall sample analysis will be introduced.
First, we combined HPPM with microdroplet injection, which can introduce a small droplet of a few tens of picoliters into a plasma excitation/ionization source, for the analysis of single cell and nanoparticles. Pulsed plasma generation and sample droplet introduction into the plasma were synchronized to provide a high- sensitivity atomic emission spectroscopic analysis. A droplet comprising Na, Ca, Mg, and K at 100 mg $L^{-1}$was analyzed using this system and the limits of detection equaled to 300, 50, 30, and 640 fg for these analytes, respectively2.
Secound, we developed an emission spectroscopic method HPPM as an excitation source to realize highly sensitive and rapid on-site detection system for impurities in hydrogen fuel utilizing a cryofocus technique for sample introduction. The optical emission from sulfur in helium (H_2S 20 ppm) at 921 nm was observed with changing the amount of H_2S introduced into the analytical system to evaluate the analytical performance of our system. As a result, it was revealed that sulfur compound of 0.004 ppm in hydrogen fuel, which is maximum allowance concentration by ISO2, can be detected when 8 L of hydrogen was loaded to the analytical system. A high-speed signal acquisition method using monochromator and digital oscilloscope was examined to improve analytical sensitivity and the results will be discussed.

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KM-4 Excitation and ionization of iron in argon and neon glow discharges: non-LTE considerations

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In a recent study of glow discharge (GD) emission spectra of titanium **[1]**, it was found that, whilst Ti(II) spectra are best described by transition rate (TR) diagrams **[2]**, for Ti(I), the Boltzmann plots, *i.e.*, relative populations of Ti(I) levels plotted in a logarithmic scale versus energy, appear to be a more comprehensive formalism. This triggered further interest in the excitation of neutral atoms in a GD. An attempt to explain GD excitation and ionization of iron will be presented in this talk. Original idea was to focus on the excitation of the Fe(I) spectrum only, but it turned out that this would be impossible without considering the ionization of iron and the neutralization of Fe^+ ions also. Hence, this study can be regarded as an extension of our earlier work dealing with Fe(II) **[3]**.

The left plot below shows an experimental Fe(I) population function in argon and neon discharges. Next to it is the Fe(I) population function in a neon discharge only, with individual levels distinguished by their spin multiplicity. Beneath that plot is a diagram of all Fe(I) levels existing in the energy range displayed (2 to 8 eV), also sorted according to their multiplicity. The population functions were calculated based on a large number of Fe(I) lines, in emission spectra measured using the vacuum high resolution VUV-Vis Fourier transform spectrometer at the Blackett Laboratory, Imperial College London. The arrow in the right plot points at a peak of the population function at 5.0 eV. This peak can be attributed to the reaction Fe + Fe^+ + e- Fe^* + Fe^*. It was found that the Fe()I populations in a GD plasma do *not* follow the Boltzmann distribution and any "excitation temperatures" reported sometimes in the literature for a GD plasma are virtually meaningless, at least in the context assumed by the LTE model.

Acknowledgement:
The spectral data were collected in July 2010 during an author's visit to the Imperial College London, financed within the MRTN-CT-664 035459 GLADNET project, under the FP6 program for Research and Innovation (Marie Curie Actions) of the EU. The author wishes to thank Prof. J.C. Pickering who kindly let us use the FT spectrometer at Imperial College to collect the spectra and prof. E.B.M. Steers†, Dr. S. Mushtaq and Dr. V. Weinstein for help with the measurements.

Keywords: iron, excitation, ionization, glow discharge, emission spectroscopy, Boltzmann plot, LTE

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KM-5 The power of micro-second detection ICP-MS for the accurate determination of nanoparticle number concentration: underpinning metrology for biomedical applications

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Measuring the number concentration of nanoparticles (NPs) in colloidal suspension is of major commercial interest for a large range of industries, such as personal care, fine chemicals, pharmaceutical and biomedical. It enables compliance with potential and existing EU regulation (*e.g.* Cosmetics 1223/2009 and Novel food 258/97) linked to the EU definition of a nanomaterial (2011/696/EU) **[1]**. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been proven to be a powerful technique for providing number concentration of inorganic nanomaterials with minimal or none sample preparation **[2]**. Therefore, there is increasing interest in using this technique for routine high sample throughput applications.

The accurate determination of nanoparticle number concentration using SP-ICP-MS with low uncertainty is facilitated by measuring the sample uptake and the sample dilution gravimetrically. There are then key remaining parameters such as the transport efficiency and the number of detected particles that have been found to significantly contribute to the overall uncertainty associated with the number concentration data. For the latter parameter, the right selection of instrument parameters (*e.g.* dwell time) plays a crucial role in eliminating the chance that particles are missed or partial ion clouds are detected and in resolving nanoparticle signals from those of the background.

This keynote lecture will address the advantages of using microsecond over millisecond detection ICP-MS for the accurate determination of number concentration of metal NPs using SP- ICP-MS. This will be illustrated through two applications including (*i*) the determination of number concentration of colloidal gold NPs for the metrology inter-laboratory comparison CCQM-P194 and subsequent characterisation of the quality control material LGC 5050 and (ii) the detection and characterisation of Ag-NPs used as antibacterial in medical devices. This requires NP measurements in the presence of relatively high dissolved Ag ion concentrations for analysis of samples relevantto toxicology and biomedical research.

Keywords: inorganic nanomaterials, microsecond dectection ICP-MS, SP-ICP-MS, biomedical applications, quality control

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KM-6 New advances in the absolute quantification of biomolecules using ICP-MS/MS and generic standards

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Current trends in Life Sciences are heading towards the absolute quantification of biomolecule(s) of interest in order to validate biomarkers, characterize biological systems, etc.. Inherent analytical features of ICP-MS have placed it as a versatile tool to address such quantification with hyphenated chromatographic (LC) separation. Generic determination of ICP- detectable elements present in biomolecules would enable their absolute quantification without resorting to specific standards.

However, ICP-MS-based quantification of biomolecules in speciation analysis has been constrained so far by different reasons. Most important one is the use of carbon containing mobile phases along most reversed-phase and HILIC separations, which significantly affect plasma ionization processes of heteroatoms. As a consequence, elemental response factors in LC-ICP-MS analysis are usually different at each moment of the gradient analysis, which render the use of a generic element-containing standard for quantification impossible. The only acceptable solution so far consisted on the use of post-column isotope dilution. Direct measurement of the isotope ratios of the target element in the compound of interest after post-column on line continuous addition of an enriched isotope solution, whose concentration and isotopic abundances are accurately known, can provide perfect correction of sensitivity changes along gradients and therefore, accurate quantification without the need for specific standards. We have extensively used this strategy to carry out the absolute quantification of the multiple protein toxins (up to 40) present in different venom samples using an enriched solution of ^{34}S and ICP-MS/MS **[1]**. Unfortunately, this strategy cannot be considered universal as it is only applicable to multi-isotopic elements, requiring in addition specific enriched isotopes for each one.

We have recently developed a novel and highly sensitive ICP-MS/MS approach for absolute quantification of every target biomolecule containing P, S, Se, As, Br, and/or I (*e.g.*, proteins and phosphoproteins, metabolites, pesticides, drugs), under the same simple instrumental conditions and without requiring any specific and/or isotopically enriched standard **[2].** Optimized and controlled addition of carbon-containing gases to the plasma leads to the correction of carbon effect in the ionization of heteroatoms. It has proved to be a simpler, more sensitive and cheaper way of addressing quantitative speciation analysis of biomolecules with LC-ICP-MS. We will compare in this work the performance of different gases (CH_4 and CO_2) in terms of accuracy (quality of sensitivity correction) and detection limits. Different quantification approaches making use of both internal and external generic standards will be critically compared as well. Definitive proposed strategy will include in situ column recovery evaluation, which is critical to assure accurate results. Finally, applicability of the proposed approach to the quantification of target biomolecules in real samples will be also shown.

Keywords: ICP-MS/MS, speciation, generic quantification

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OM-01 Multielemental analysis with plasma pencil

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Plasma pencil is a capacitively coupled plasma discharge (CCP) at 13.56 MHz operated in a quartz tube (i.d. 2 mm). It was originally designed for modification of surfaces of various objects of cultural heritage. Argon is most commonly used as plasma gas but other gases (e.g. helium) and their combinations are usable as well. Typical operational plasma gas flow rate is 4 l/min, carrier
0.25 l/min and forwarded power 140 W.

In the field of analytical chemistry its potential to be an alternative excitation source for determination of elements concentrations in solutions is investigated [1, 2]. Liquid samples for the plasma pencil are processed by the same way as for inductively coupled plasma (ICP). A peristaltic pump, concentric nebulizer and a double pass Scott spray chamber are used. Elements of 1st and 2nd group of the periodic table can be easily excited and also some other metals of which melting and boiling temperatures are not high related to the pencil plasma were studied. Copper and zinc emission lines were already studied under various conditions and under the influence of easily ionisable elements (EIE). It was shown that intensities of their atomic lines are suppressed or less frequently enhanced by the presence of EIE (1st and 2nd group elements of the periodic table) in the sample solution [3]. The suppression was also found in the presence of nitric acid.

To find out if the plasma pencil can be used as an alternative excitation source real drinking water samples were analysed and matrix effects were studied. The standard addition method and the calibration line method were used for determination of sodium, magnesium, potassium and calcium concentration. To achieve the most accurate results of the water analysis and to compensate for possible interelemental influence, several calibration curves from different single element and multiple element standard solutions were used. ICP-OES was also employed for the same experiments as a validation method. Based on the data evaluation and interelement corrections it can be concluded that the results of these two methods do not differ significantly.

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Keywords: capacitively coupled, plasma, pencil, ICP, OES, matrix effect, calibration, standard

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OM-02 Concentric-electrodes atmospheric pressure glow discharge for the analysis of volatile organic compounds

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The publications of Cooks et al. on a new analytical technique based on desorption and ionization of a sample in ambient conditions (DESI) and Cody et al. on their direct analysis in real time (DART) source, opened a new branch in the field of analytical chemistry: the ambient desorption ionization mass spectrometry (ADI-MS). Since these first publications, the ADI-MS has known a rapid grown up from a fast and easy qualitative screening to accurate quantification tool **[1]**.

The principle of this new method is based on direct sampling, desorption and ionization of analytes in open air at ambient conditions (atmospheric pressure and room temperature). The samples are analysed with no or little pre-treatment from their native state before the analysis itself. Moreover, as sample desorption/ionization takes place at atmospheric pressure, the collisional processes with air species allow the dissipation of excess energy and thus the analyte fragmentation is diminished **[2]**.

Different ionization sources designs, their characteristics as well as the large range of possible applications, have been investigated in many publications. The rapid direct analysis of several compounds with low detection limits and adequate reproducibility have been demonstrated in these works. Among the different sources, a significative number is electric discharge based, as for example DART, low temperature plasma (LTP) or flowing atmospheric pressure plasma (FAPA).

The source presented in this work is a FAPA source composed by two tubular electrodes placed in a concentric geometry **[3]**. With this distribution, the introduction of gaseous samples through the internal electrode directly in the afterglow region is possible. In this present work, the reactive species generated by this concentric FAPA source have been studied and the experimental conditions have been optimized. Finally, the analytical potential of this FAPA source has been studied for the direct analysis in air and breath of volatile organic compounds (VOCs) such as benzene, toluene, isoprene, furan or acetone.

Keywords: FAPA, APGD, GD, glow discharge MS

Acknowledgment
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OM-03 In-cell chemistry to overcome spectral overlap in ICP-MS/(MS): the next step

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Trace elemental analysis at increasingly lower levels is of high relevance in various fields, such as environmental and food chemistry, medicine and/or materials science. Inductively coupled plasma mass spectrometry (ICP-MS) can be seen as the most powerful technique for ultra-trace element determination in a large variety of sample types. However, ICP-MS also suffers from drawbacks, the occurrence of spectral interferences being the major one.

As a result, many different strategies to overcome spectral overlap have been developed over the years, but the use of collision/reaction cell (CRC) technology can be regarded as the most widely used approach. Especially, tandem ICP - mass spectrometry (ICP-MS/MS) enables one to deal with spectral overlap in a very effective way **[1]**. The better control over in-cell chemistry also enables the use of highly reactive gases, often relying on the monitoring of molecular ions instead of atomic ions **[2]**. The molecular ions are mass-shifted, whereby the new mass-to-charge (m/z) ratio at which the analyte ion signal is measured can be cleared from other ions.

This presentation will address such approaches in multi-element ultra-trace analysis, and when monitoring ultra-fast transient signals, *e.g.*, in the case of single-particle ICP-MS analysis **[3].**

Keywords: ICP-MS/MS, chemical resolution, multielement, nanoparticles, transient signals

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OM-04 Uncovering beryllium line with forbiden component

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Beryllium is uniquely strong and light element, it has six times the specific stiffness of steel and at the same time it is one-third lighter than aluminum which makes it suitable for a wide range of applications: aerospace, information technologies, energy exploration, medical and other. Beryllium is naturally occurring element in metal-poor stars **[1]**. Also, beryllium has been chosen as the element to cover the first wall of international thermonuclear experimental reactor (ITER) **[2]**. But still, spectroscopic investigations and Stark parameters studies are almost exclusively limited to Be(II) resonance lines at 313 nm. The reason for the lack of experimental data may be found in the toxicity of beryllium.

During this research novel plasma source was constructed in order to safely record the beryllium lines in laboratory condition **[3]**. Beryllium lines appeared as a result of the ablation of the discharge tube made of ceramic, BeO. The presence of dust particles was also observed. It is found that the optimal conditions for Be spectral line shapes measurements are achieved with C = 5 F, U = 7 kV, gas Ar +3% H2, p = 1.2 mbar. The electron density, Ne, and temperature, Te, were determined by using the iterative method. The electron number density during plasma afterglow was estimated using the peak separation Δps of the hydrogen Balmer beta line and the electron temperature is determined from the ratios of the relative intensities of Be spectral lines emitted from successive ionized stages of atoms.

From this pulsed discharge plasma, several beryllium lines were observed and amongst them the Be(II) 436.09 nm line with a forbidden component detected for the first time, to the authors knowledge. This result partially fills the gap between the investigations of this type of transitions along lithium isoelectronic sequence, with already published data for Li(I), C(IV), and N(V).

Keywords: beryllium lines, forbidden lines, optical emission spectroscopy, spectral line shapes, plasma sources, dusty plasma

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OM-05 Electrospray single-cell inductively coupled plasma mass spectrometry (ES-SC-ICP-MS)

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Single-cell inductively coupled plasma mass spectrometry (SC-ICP-MS) is a powerful technique for the determination of the elemental contents of individual cells. The distribution of cellular elemental contents can be used to evaluate the physiological state1 and the heterogeneity of the cells2. Typical sample preparation procedures for SC-ICP-MS involve repeated centrifugation and resuspension of the biological cells in water or buffer solutions to remove interfering elements in the culture solutions. However, the biological cells suffer from severe mechanical stresses during the centrifugation process 3, as well as osmotic stresses across the cell membrane due to the difference in electrolyte concentration between the cell and the cleaned medium4. These stresses may induce changes in the elemental contents of the cells and cell. To minimize the stresses introduced to the sample cells during the preparation procedures, a novel sample introduction system by electrospray is proposed. The system consists of a graphite electrode (diameter = 4.52 mm, tip angle = 45 °) and a counter ring electrode. A 2 L aliquot of sample cell suspension is placed on the tip of the graphite electrode. A potential ranging from 7 kV to 10 kV was applied to the graphite electrode to produce a spray. The spray current was 1.5 A or less. The spray of a 2 L aliquot of cell suspension can be sustained for a few minutes, which is long enough for a typical time-resolved SC-ICP-MS measurement. The spray was visualized by laser scattering (wavelength = 532 nm). The spray angle was approximately 70° and is insensitive to the applied potential and the distance between the graphite tip and the counter electrode. The sprayed cells appeared to be intact and well-separated as individual cells. Characteristics of the sample introduction system will be presented.

Keywords: Electrospray, single-cell inductively coupled plasma, mass spectrometry, SC-ICP-MS, sample introduction

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OM-06 New possibilities of time-of-flight mass spectrometry with pulsed glow discharge in combined hollow cathode

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Two new variants of a pulsed direct current glow discharge time-of-flight mass spectrometry (GD-TOF-MS) method are considered. First one is quantification of elements with high ionization energy (fluorine, chlorine and oxygen) in solid samples and second one – direct determination of VOCs in ambient air and exhalation.

If compared to other common inorganic mass spectrometry ion sources, the use of pulsed DC-GD-TOF-MS under low repelling pulse delays enables ionization of the atoms with high ionization potentials. The mechanism of ionization is related to the collision of the CHC sputtered material with high-energy electrons, generated on the front of the pulses. Under the most commonly used pulse period of 300 s, prior to the following pulse there is a high concentration of the sample's atoms in the area between the edge of discharge cell and mass spectrometer's sampler. These atoms diffuse through the sampler into the non-collision zone between the sampler and the skimmer. The following pulse generates the discharge front with high power release (current of 1.0-1.5 A, voltage 1300-1400 V) within a very short period of time. Consequently, a high-energy electrons beam injects into the sampler and ionizes the atoms and molecules in the non-collision zone. Owing to the long free run of the particles in the space between sampler and skimmer, the generated ions can reach the mass spectrometer's detection system without colliding. Thus, the most highly reactive particles such as $^{19}F^+$, $^{16}O^+$, $^{35}Cl^+$ can be both generated and detected **[1,2]**.

The possibility of direct determining VOC in ordinary air using time-of-flight mass spectrometry with a DC pulsed glow discharge is also considered. We note that direct determination of VOCs in exhaled air can be used, for example, to solve such an important problem as early diagnosis of lung cancer. In the experiment, the possibility of detecting VOCs when introducing air with the vapor of a series of compounds into an argon flow entering a discharge cell with a copper hollow cathode was investigated. It was expected that the main mechanisms for the formation of analytic ions will be determined by two reactions: Penning ionization and proton transfer ionization. However, the most effective process was the process connected with the association reaction:

$$Cu^+ + M = CuM^+$$

The high efficiency of this process is associated, first of all, with a high concentration of copper ions at a relatively low probability of dissociation of the detectable compound in a pulsed glow discharge in a hollow cathode. A high concentration of copper is determined by the high rate of sputtering of copper, even in the presence of a significant amount of oxygen and water in the discharge, which enter the discharge cell as a part of the air sample. It has been shown that the above considered mechanism of ionization by a package of high-energy ions is also effective in the case of VOC ionization.

The report presents these techniques and demonstrates the possibility of switching the ionization mechanism by changing the discharge parameters and settings of the mass spectrometer.

Keywords: mass spectrometry, pulsed glow discharge, high ionization energy elements, volatile organic compounds, direct determination, ionisation mechanisms, combined hollow cathode

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OM-07 Equilibrium chemistry of boron halides in plasma chemical reactors

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High purity halides of III-VI group elements, especially chloride and fluorides, are used in gas phase technologies for obtaining high purity materials and coatings. The reduction of halides in hydrogen-halide mixtures can be achieved in various discharge plasmas, *e.g.* inductively coupled, ark, and even laser induced plasmas. Existing models of such plasmas are not sufficiently accurate to predict a yield of the targeted compounds and to describe the plasma processes involved in formation of these compounds. Besides, a construction of costly plasma-chemical reactors can be alleviated by the prior modeling of plasma processes that may occurr in such reactors.

A goal of this work is to extend the model, which was initially developed for laser induced plasmas **[1]**, to plasmas used in chemical reactors, in particular, the inductively coupled RF discharge plasma **[2]**. The model predicts equilibrium chemical compositions of reaction mixtures as functions of plasma temperature and stoichiometry of reactants. The mixtures investigated are $BCl_3/H_2/Ar$ and $BF_3/H_2/Ar$ where Ar serves as the plasma-forming gas and H_2 as a binding agent

which binds the active species Cl and F and Cl^- and F^- containing intermediates to produce gaseous B and its condensate. An additional goal is to obtain information about intermediate reaction products for different ratios of BCl_3/H_2 and BF_3/H_2 and at different temperatures and different Ar flow rates.

It is found that the desired components B and B_2 appear at appreciable concentrations of > 0.1% and 0.01% respectively only at temperatures above 3000 ˚K. It is also established that the effect of charged species on the reaction products is miniscule for temperatures below 5000 ˚K. The expected yield of boron as a function of the original mole fraction H_2/BCl_3 and H_2/BF_3 is calculated. The mole fractions are varied in the range 0.1-1000 and the temperature in the range 1000-10000

˚K. It is shown that the yield of boron increases with increasing the molar ratio H_2/BCl_3 and H_2/BF_3 up to 100 in the temperature range 2000-5000 K. At higher temperatures, T> 5000 ˚K, the boron concentration reaches its maximum and does not depend on the concentration of hydrogen; all molecules dissociate and chemical reactions proceed only between charged particles (mostly elemental ions) and electrons. The calculated plasma parameters and composition are compared with experimental data obtained by optical emission spectroscopy. The calculated plasma temperature and electron density are shown to be in good agreement with the measured ones.

Keywords: Plasma chemistry, equilibrium chemistry, plasma modeling, plasma chemical reactors

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OM-08 Quantification strategies for the analysis of major and minor components by means of pulsed glow discharge time-of-flight mass spectrometry

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Pulsed glow discharges (PGDs) coupled to time-of-flight mass spectrometry (TOF-MS) offers great potential for depth profile analysis of materials, as it allows high acquisition rates and good mass resolution, together with depth resolution in the nanometer range. Moreover, thanks to the low intrinsic matrix effects of glow discharges, it can be obtained not only qualitative (signals versus sputtering time) information but also quantitative results (concentration versus sample depth) **[1]**. Nevertheless, there is still a lack of analytical quantitative approaches to achieve this last aim, especially when dealing with PGD sources.

In this communication, we will present different quantification strategies for quantitative depth profile of major and minor elements, taken advantage of the intrinsic characteristics of the PGDs by means of PP-TOF-MS. Also, sensitivity improvements obtained thanks to the possibility to blank major components will be discussed. Within this context, we have developed quantification procedures for two types of samples: (i) stainless steel substrates contaminated with low concentrations of inactive rare earth elements (REEs) to investigate the penetration of contaminants, and (ii) electrodeposited multilayers and compositionally modulated alloys consisting of Cu and Ni- Cu layers that need to be characterized in terms of layer thickness and composition. Despite the afterglow region is the preferred region as its sensitivity is higher as compared to plateau and prepeak, saturation issued within major components can occur and so, two alternative signals to this major analyte measured in the afterglow (while keeping the rest of the analytes in such region to maintain sensitivity for minor components) will be here proposed.

Keywords: time of flight mass spectrometry, materials, depth profile, quantitative analysis

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OM-09 The use of a multiple inlet nebulizer in ICP- based techniques for spectrochemical analysis

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The development and characterization of new sample introduction systems based on liquid nebulization is a field of continuous innovation with an open end. The main purpose of this field is to develop new nebulizers able to generate aerosol with good characteristics not only from model solutions with well controlled matrix, but also from real world samples, usually complex matrix samples (*e.g.*, high salt-content samples, organic samples, or digested samples). However, analyses of complex matrix samples by ICP-based techniques usually suffer from problems other than those exclusively related to aerosol quality, denoted as matrix effects. Elimination of such matrix effects, caused by both spectral and non-spectral interferences, is, undoubtedly, of special interest for analysts.

Recently our research group has introduced a new MultiNeb® **[1].** The MultiNeb® nebulizer opens new possibilities for spectrochemical analysis by ICP-based techniques, allowing the implementation of on-line calibration methodologies and on-line chemical vapor generation, in an easy way. Examples of applications to the analysis of typical complex matrix samples such as high salt-content samples (*i.e.*, estuarine water), organic samples (*i.e.*, petroleum products and biofuels) and high inorganic-acid-content samples (*i.e.*, digested samples) will be also discussed.

Keywords: Multiple nebulizer, online calibration, online chemical vapor generation

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OM-10 Mass spectral imaging of iodinated contrast agents in biological tissue samples by means of LA- FAPA-MS

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Mass spectrometry imaging (MSI) has become a valuable tool for analyzing the spatial distribution of analytes in complex samples. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is the method of choice in order to investigate elemental distributions particularly due to the high spatial resolution, minimal sample preparation, and excellent sensitivity offered by this combination. MSI of molecular species is often performed with matrix-assisted laser desorption/ionization (MALDI-MS) and secondary ion mass spectrometry (SIMS) and is susceptible to ionization matrix effects and reliant upon a cumbersome sample preparation. The desire to simplify mass spectral analysis led to the development of ambient desorption/ionization mass spectrometry (ADI-MS) in the past decade. In 2013, Pfeuffer *et al.* introduced a new ADI-MS source called halo-flowing atmospheric pressure afterglow (halo-FAPA). Here, molecules are desorbed/ionized in the afterglow region of a halo-shaped atmospheric pressure glow discharge sustained in helium.

The focus of this work lies on the application of a novel imaging technique based on halo- FAPA-MS. This technique was employed for the investigation of the accumulation and clearance of iodinated contrast agents (ICAs) in kidney samples. For this, 10 m thick cryosections of rat kidneys were prepared 24 and 48 hours after single administration of an ICA and subsequently analyzed by LA-halo-FAPA-MS. By use of laser ablation, good spatial resolutions of around 50 µm and a high reproducibility of sample introduction were achieved. Furthermore, complete ablation of the sample allows for quantification by use of matrix-matched standards based on gelatin. Halo-FAPA post- ionization was tuned with respect to operating parameters such as gas flow rates and discharge currents to attain high sensitivity in MS analysis. The presented technique was employed for elemental bioimaging of the iodine distributions in samples of rats treated with two different ICAs. It could be shown that LA-FAPA-MS is a versatile technique for mass spectral imaging that can be easily hyphenated to different mass analyzers due to its modular design and, in certain cases, offers a simple alternative to LA-ICP-MS.

Keywords: flowing atmospheric pressure afterglow, laser ablation, bioimaging, iodinated contrast agents

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OM-11 About detectability and detection limits in single particle ICP-MS

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) offers unique features for the detection of particles in liquid suspensions, as well as for their quantification and characterization. Like any other analytical method, SP-ICP-MS has limited detection capabilities. Because of the different types of information that SP-ICP-MS can provide, these capabilities can be related to concentrations, but also to mass of element per particle (and particle size when additional informations about shape, composition and density of the particles are available). Moreover, concentration information involves both number concentration as well as mass concentration of particles and dissolved species. In any case, these detection capabilities can be quantified as the corresponding limits of detection (LOD).

In spite of its broad use, LOD remains a complex topic and some confusion exists around it, which is a consequence of the different approaches available for LOD estimation. This is also the case in SP-ICP-MS, although aggravated by the following facts: (i) SP-ICP-MS is a counting technique, governed by Poisson statistics, both with respect to the signals (counted ions) and the particles; (ii) blanks and baseline levels can be very close to zero, although they can also show high values; (iii) in a typical measurement process the occurrence of baseline events is larger than that of particles (at least one order of magnitude) and (iv) both concentration as well as size (or mass of element per particle) LODs must be considered.

SP-ICPMS is an emergent methodology, which still lacks harmonized metrological protocols, as well as rigourosly validated methods. This is the case of the protocols for discrimination of particle events, which have to be based in robust limits of decision, or the calculation of the different limits of detection, which must involve harmonized expressions to allow reliable comparisons between methods and instruments.

The objectives of this contribution are to highlight the peculiarities of detectability in SP- ICP-MS, as well as to propose criteria and expressions for the calculation and application of the different limits of detection (size, number, mass), in an attempt to open a process of harmonization in the SP-ICP-MS community about these topics.

Keywords: single particle ICP-MS, nanometrology, limit of detection, nanoparticle, nanomaterial

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OM-12 Pros and cons for the use of ICP-MS in proteomics

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Proteomics is a field dominated by the use of organic mass spectrometry. The use of elemental mass spectrometry in proteomics so far is limited. This presentation tries to summarise some of the potential reasons why elemental mass spectrometry does not have a larger input into proteomics and where it could potentially make a contribution. With the advent of ICP-QQQ and the long established high resolution instruments this can not be only due to detectability issues. Both types of instruments allow sensitive determination of sulphur and phosphorus. These elements are both of intense interest in proteomics, since the redox state of sulphur containing amino acids and the phosphorylation of specific amino acids are key to post translational protein modifications in a wide range of biological systems.

Keywords: peptide analysis, ICP-MS, sulphur, phosphorus

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OM-13 Multi-spray CGrid nebulizer for perfect matrix- matching in single particle ICP-MS

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a promising method for measuring size distributions and number concentrations of inorganic particulate matters, being applied to evaluation of industrial and environmental particulate matters such as nanoparticles and suspended particles. However, several technical issues still remain with respect to ensuring analytical reliability and comparability with other measurement techniques. One of major issue is to compensate for matrix effects caused with solvents, acids, surfactants, and concomitants in particle suspensions or ionic standard solutions, resulting large difference of signal responses in the measurement of different suspensions and solutions. Indeed, ionic standard solutions are frequently used for correcting the transport efficiency of particles into the plasma and calibrating the signal response to mass amount of elements, but these solution conditions hardly match with those of particle suspensions. Matrix matching is the best way to compensate the matrix effect, but it is difficult to prepare both suspensions and ionic solution (or particle standard suspension) with the same solvents and other components. An in-line mixing of a sample suspension and an ionic standard solution is an alternative approach for matrix matching. However, non-polar organic solvent and water solution hardly mix in homogeneous even though a mixing device are used for accelerating the mixing. For realizing a perfect matrix matching for various matrices including non-polar organic solvents, microflow type multi-spray CGrid Nebulizer (m-CGrid) was newly designed. The m-CGrid can nebulize two independent liquids without premixing, due to a unique structure. It has two independent liquid-flow capillaries inside one nozzle and a grid screen putting on the hole of the nozzle. The grid acts as both a flow damper and sieve, resulting well-mixing of liquids and nebulizing gas inside the nozzle and further breaking-up into small droplets. The primary aerosols obtained in the range of 0.01 to 0.10 mL.min^{-1} of the liquid flow rate were quite fine ($D_{3,2}$: 2.1-2.3 mm for both channels), and the signal intensities obtained with two liquid channels closely matched with a good precision (< 2% in 2 min measurement) at 0.01 mL.min $^{-1}$ of both liquid flows. These performance are much suite not only for constructing a total consumption sample introduction device but also for matrix matching in SP-ICP-MS.

Keywords: nebulizer, SP-ICP-MS, matrix matching, nanoparticles

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OM-14 Selenometabolites and selenoproteins mother- offspring transfer through human breast milk and cord serum by column switching inductively coupled plasma triple quadrupole mass spectrometry

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Human breast milk can be considered an ideal food for babies that contains macro- (proteins, lipids, carbohydrates) and micro-nutrients (vitamins, enzymes, minerals) at adequate levels of concentration, and the chemical composition varies over time with respect to colostrum (days 1-3) to mature milk (days 14-28 after delivery). On the other hand, selenium is an essential micronutrient very important during pregnancy with a very narrow range between deficiency and toxicity, also related with its chemical form. The active center of selenoproteins (with selenocysteinyl residues) like glutathione peroxidase and other selenoenzymes is (-SeH), but selenium can be present also in living body as selenium containing proteins (with selenomethionyl residues, ie Selenoalbumin), inorganic selenium, selenoamino acids and methylated selenium **[1]**. The selenium specie most abundant in the bloodstream is selenoprotein P (SeP) and its concentration is a good indicator of Se status in humans, while extracellular glutathione peroxidase (eGPx) is a complementary marker of selenium status in several clinical studies. Moreover, Se- proteins are interrelated, because Se bound to albumin (SeAlb) is assumed to be transported to the liver for new synthesis of SeP and GPx that are then released into the bloodstream. The concentration of selenium in human serum is about 90 $ng.g^{-1}$ and this elements occurs as SeP> Selenoalbumin (SeAlb)> GPx> SeO32- **[2]**.

A method for the simultaneous speciation of selenoproteins and selenometabolites in human serum and breast milk has been developed based on 2D high performance liquid chromatography (size exclusion and affinity chromatography) hyphenated to inductively coupled plasma triple quadrupole mass spectrometry (ICP-MS/MS). The method allows the quantitative simultaneous analysis of selenoprotein P (SeP), extracellular glutathione peroxidase (eGPx), selenoalbumin (SeAlb) and selenometabolites in human serum and breast milk using species-unspecific isotope dilution (SUID) **[2]**. This analytical method has been applied to maternal and umbilical cord sera at the time of birth (83 couples). Additional measurements of serum SeP concentration and of serum GPx enzyme activity were carried out using ELISA. Total Se concentration was significantly higher in maternal serum than in cord serum. SeAlb concentration was significantly higher in newborns, whereas SeP and GPx concentrations were significantly higher in mothers. The differences cannot be explained by simple diffusion; specific transfer mechanisms are probably involved. In addition, selenoproteins and selenometabolites have been identified and quantified in breast human milk. In this biofluid, selenium occurs at glutathione peroxidase (4-32% total Se)> selenocystamine> selenocystine> selenomethionine at 26, 18, 15 and 17 g L^{-1} in colostrum (0-5 d), transitional milk (6-21 d), mature milk (1-3 months) and late lactation (> 5 months), respectively.

Keywords: Selenium, selenoproteins, human breast milk, cord serum, offspring transfer, triple quadrupole inductively coupled plasma mass spectrometry

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OM-15 A novel data processing strategy for quantification of nanoparticles and dissolved metals in mixtures with SP-ICP-MS and microsecond time resolution

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) with a quadrupole detector is widely used for sizing and counting nanoparticles (NPs) in aquatic matrices; however, there are still some issues that are needed to be addressed, namely, the quantification of dissolved ions and NPs in mixtures. It is common that ionic metals are present together with NPs or an isotope that is used for NPs detection has a high natural background (BG) or interferences. In these cases, the NPs detection is hindered due to the high BG and its deviations.

To address these limitations, a data processing strategy using 5 s home-built data acquisition system **[1]** was developed. In this presentation, on an example of silver NPs in the presence of silver ions (Ag^+) it will be shown how it was possible to detect NPs with the BG signal from one of the silver isotopes reaching up to 1,000,000 cps. Additionally, Ag^+ could be quantified in the presence of NPs and the features (possible matrix effects, data processing) of this procedure will be discussed. The developed **[1]** and refined data processing algorithm with a special focus on choosing suitable parameters for NPs extraction will be introduced. The new strategy allowed to considerably increase the continuous BG tolerance and decrease the NPs size detection limits in the presence of continious BG.

As a result of the study, a simple and user-friendly algorithm to process the data obtained from analysis of NPs and ionic metals in mixtures, NPs containing high natural BG or interferences during SP-ICP-MS measurements that can be implemented to any detected isotope will be presented.

Keywords: SP-ICP-MS, microsecond time resolution, data processing, dissolved

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OM-16 Potential reference measurement procedures to quantify metalloproteins in CSF and serum

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Alzheimer's disease (AD) is one of the main challenges for the healthcare systems of aging societies worldwide. Metalloproteins are likely to be involved in or released by the body during the development of AD. Reliable and comparable results are the basis for the investigation of changes in the proteome due to different health conditions. Nevertheless, for many metalloproteins the results achieved with different routine measurement procedures or in different laboratories vary widely, thus, hampering medical insights and the development of treatments.

The metalloproteins discussed to be involved in the development of AD are the iron transport and storage proteins (transferrin (TRF) and ferritin (FER)) as iron is important for the function of the brain. Besides these proteins, ferroxidases such as ceruloplasmin (CER) are also involved in iron regulation by oxidising iron to the less toxic ferric state which can be bound, for example, by TRF. Furthermore, CER is a copper storage protein and copper is thought to be involved in the formation of b-amyloid oligomers. As it seems that damage of the neurons through oxidative stress is involved in the process of AD, superoxide dismutase (SOD) is also a promising candidate for monitoring the progress of the disease.

To achieve traceability of the results, species-specific double isotope dilution mass spectrometry (IDMS) methods are developed for the quantification of these metalloproteins via their metal content using inductively coupled plasma mass spectrometry (ICP-MS) for the detection. The coupling with liquid chromatography ensures the separation of the analyte from interfering matrix. A challenge when using IDMS in clinical analysis is the production of the isotopically labelled version of the analyte protein. In most cases, such a protein is not commercially available. Different approaches are used depending on the binding form of the metal in the protein. In case of easily exchangeable metal ions such as in SOD and CER, the metals can be removed from the natural protein by lowering the pH and dialysis. For SOD, the process can be accelerated by using a complexing agent such as ethylenediaminetetraacetic acid (EDTA). In case the isotopic labelling is intended via heteroelements such as sulphur, the spike protein has to be produced recombinantly. This approach is used for quantifying FER as a reproducible saturation of the protein with isotopically enriched iron is difficult. In all cases both, reference and spike material required for double IDMS, have to be characterised thoroughly. Various methods such as elemental and molecular MS, gel electrophoresis and optical methods are applied in our laboratory for this characterisation.

Keywords: reference measurement procedures, metalloproteins, serum, cerebrospinal fluid

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OM-17 Double-Viewing-Position SP-ICP-AES

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Single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has widely been used for the characterization of nanoparticles (typical size range = 10 – 103 nm). However, calibration with standard solutions for particle-size determination sometimes introduces systematic error as the sensitivity (atoms.count^{-1}) of nanoparticles is generally lower than that of standard solutions **[1,2]**. With an appropriate correction factor, calibration using standard solutions is possible but is only applicable over a small size range (3 orders of magnitude in mass) **[3]**. The main reason is that particle vaporization is not instantaneous and large particles are incompletely vaporized in the ICP.

A double viewing position single particle inductively coupled plasma optical emission spectrometry (SP-ICP-OES) has been developed to study particle vaporization in the ICP **[4]**. Polydisperse Yb_2O_3 particles (200 – 2000 nm) were used as test particles. The emission at two positions (8.5 and 19.5 mm above the load coil (ALC)) were measured to give a pair of temporal emission peaks for each particle (double-peak). Correlation of intensities of the two peaks in a 2D plot shows a large variation in intensity at 8.5 mm ALC. As the boiling point of Yb_2O_3 is approximately equal to the ICP gas temperature at 8.5 mm ALC, the degree of vaporization (DOV) of the particles is low. In addition, the temperature at the rim of the ICP central channel is 400 °K higher than that at the center, leading to a large variation in DOV. The temporal peaks with exceptionally small intensity also show asymmetric peak shape due to poor particle vaporization. Moving to higher observation position, adding helium to the carrier gas flow, or confining the particles to the rim of the ICP central channel using a sheath gas device, effectively increases the DOV and reduces the variation in intensity. In the presentation, experimental and simulated temporal profiles of the double-peaks and the correlation plots will be examined. Criteria of selecting optimum sampling position will also be discussed.

Keywords: ICP-OES, single particle measurement, viewing position, sampling depth, boiling point, gas temperature

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OM-18 Screening s of metallophores content and metal transport in microorganism by the use of isotopically enriched species

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Several organisms, especially microorganisms, are producing metal-binding molecules (metallophores) to scavenge metal ions in their close environment as they are essential for their growth. More and more, metallophores, included at trace levels, are found to play a key role in competition for metal ion in metal-limited environment. Because of this, a sensitive, specific, accurate and precise method to evaluate their concentration is of utmost importance. To achieve this goal, the difficulty that represents the quantification of a compound that is in constant equilibria with its complexed form has to be overcome. Method development of such a method was tested quantifying the metallophore, staphylopine. One conclusive strategy was to add a slight excess of metal ions to samples and standards to have them saturated and stable in their complexed forms during chromatographic separation. Because of potential coelution with other biomolecules binding the residual added metal ions, quantification by HPLC-ICP-MS coupling was possible only when sample matrix was simple and/or when metallophores were present at significant concentrations (> 10 mol.L^{-1}). However, HPLC-ESI-MS (high resolution) coupling allowed the quantification of metallophores at low concentrations (nmol.L^{-1}) but with lower precision and accuracy. Therefore, to solve these issues, isotopically enriched metallophore ($^{13}C_3$-staphylopine in that case) was synthetized, its concentration was checked by HPLC-ICP-MS and it was then used for sample quantification by HPLC-ESI-MS. While following metallophore production and transport is a first interesting step, tracking metal transport between the cells and their environment has also to be evaluated. Indeed, to maintain metal homeostasis, metal content in cells is controlled simultaneously by several importers and exporters, which can make harder the evaluation of the role of an individual transporter. In that sense, the addition of isotopically enriched metal ions to culture media during cell culture is a powerful tool to distinguish import from export. Therefore, can be evaluated more precisely the impact on metal transport of the mutation of a particular transporter gene or the presence of a particular molecule in the culture media.

Keywords: metallomics, metallophore, siderophore, speciation, isotopically enriched species, HILIC

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Mating with an elephant in atomic spectrometry

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Elephants may stroke each other with their noses before the male mounts the female from behind, rising nearly vertically as they mate. While elephants do not mate for life, a female may regularly like to mate with the same male, and "buyers" are sometimes seen being guarding of females!

Inductively coupled plasmas (ICPs) are elephants! No one studying atomic spectrometry one hundred years ago could have imagined the grandly conceived future explorations that are being conducted now in plasma spectrometry, particularly with ICPs. It was G.E.F. Lundell in 1933 who defined how elemental analysis must be conducted. He stated that certain methods of chemical analysis "are about as helpful to the analyst as the method for catching a bird which the old folks used to recommend to children-namely, to sprinkle salt on its tail. To do that, one obviously must have the bird in hand, and in that case, there is no need for the salt."

To highlight the lack of accurate and straightforward techniques of chemical analysis, Lundell besides asserted: "There is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone. The rub comes in because elements never occur alone, for nature and man both frown on celibacy. Methods of determination must, therefore, be judged by their selectiveness. It is in this respect that most methods are weak, and improvement must come".

One wonders what to admire most in Lundell, the psychological perception for the advancement of ideas, the sureness of scientific reasoning, the deep-felt physical acumen, the ability for explicit, systematic presentation, the complete treatment of the subject matter, or the sureness of decisive appraisal.

It was an article by Lundell that led me to the late Professor Velmer Fassel (Iowa State University and Ames Laboratory) who eventually became my postdoctoral mentor. At a major conference, Velmer spoke in honor of Professor James Winefordner who had received a significant award. As was his usual practice, he critically assessed Professor Wineforder's publications and stated that Jim's most important article was a review article that he wrote with his postdoc, Linda Cline. His highly critical tone annoyed the audience to the extent that only one person stayed in the hall to congratulate Velmer, for what I described as "an excellent lecture". Puzzled, he stated: "No one liked my speech other than you!"

Being fascinated by his speech, I told him, "I would like to join your group for the sole purpose of investigating the inductively coupled plasma as an atomization source for atomic fluorescence spectrometry (AFS). This was an unusual proposal considering that Velmer was forcefully opposed to the use of AFS! In puzzlement, he agreed! After publishing a single article, ICP-AFS was commercialized by the Baird Corporation. This was before excellent studies on ICP- MS by Professor San Houk and coworkers, then and now at the Iowa States University and Ames Laboratory. Indeed, ICP-AFS is more selective than ICP-atomic emission spectrometry and offers better detection limits for some, but not all elements. With the advent of ICP-MS, Baird Corporation ended the fortune of ICP-AFS!

After the postdoctoral studies, I joined the faculty at the Sharif University of Technology, in Tehran Iran and worked there during 1975-79. Since 1975, our research has been centered on plasma spectrometry for trace, ultratrace, isotopic, and speciation analysis of materials, such as nuclear wastes and semiconductor materials.

Our expertise has been focused on fundamental studies, modeling, simulation of plasmas and aerosol systems, development of diagnostic systems for exploring plasmas and aerosol systems, studies of smart plasmas and smart aerosols, instrument design, and the applications of aerospace, mechanical, electrical engineering, theoretical astronomy, and optics to the chemistry and the physics of novel plasmas, and cancer research, pharmacology, medical sciences, forensic science, and engineering. The techniques developed by several groups, including ours, have revolutionized the practice of analysis and led to the development of new devices, such as cell phones, high-speed laptop computers, and other high-storage devices. In my view, among all investigators in plasma spectrometries, in addition to Professor Houk, Professor Gary M. Hieftje, Professor Detlef Günther, and Dr. Richard Russo, have conducted the most significant fundamental, diagnostic, and practical applications. Prior and current studies not only have addressed challenging problems, but they have been proven vital for tackling likely difficulties that could arise in the future. These subjects will be discussed during my talk. Further, I will describe exciting possibilities in the development of new plasmas not being addressed by our research community.

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MP-1 Study on carbon-induced signal enhancement in ICP-MS: an approach from a spatial distribution of analyte signal intensities in the plasma

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Carbon-induced signal enhancement of hard-to-ionize elements with first ionization energies (IE) in the range about 8 to 12 eV is a well-known phenomenon at elemental analysis by using inductively coupled plasma mass spectrometry (ICP-MS) and mechanism of this phenomenon has been studied. However, the spatial shift of analyte ion (M^+) density zone in the ICP has not been discussed enough in these studies, despite carbon matrices greatly influence spatial position of the zone.

In the present study, carbon-induced signal enhancement was studied in detail, taking the spatial shift of the zone into consideration to obtain further insight into the mechanism. Spatial intensity distribution in the ICP and axial intensity profiles of M^+ were obtained by measuring elemental sample solutions with or without 5% (*v/v*) 2-propanol (IPA) matrix. The results showed that 5% (*v/v*) IPA significantly spread M^+ intensity distributions in particularly axial direction toward a sampling cone. Therefore, enhancement factor (EFsum) was obtained for 25 elements by dividing a sum of analyte signal intensities in the range of axial sampling position of 4 to 15 mm obtained with 5% (*v/v*) IPA matrix by a sum without 5% (*v/v*) IPA matrix as an index to evaluate signal enhancement.

Although significant signal enhancements were observed for $^{31}P^+$, $^{75}As^+$, and $^{78}Se^+$, there was no clear relationship between EFsum values and IE values of 25 elements. The axial intensity profiles and the EFsum values of $^{31}P^{16}O^+$, $^{75}As^{16}O^+$, $^{75}As^{16}OH^+$, and $^{78}Se^{16}O^+$ were also obtained to reveal an influence of 5% (*v/v*) IPA on atomization process of P, As and Se. Signal enhancements were observed for all these ions. The result implies an existence of a novel mechanism involved in carbon-induced signal enhancement; co-existing carbon accelerate atomization process prior to ionization process of the analyte. Both the acceleration of atomization process and the increase of analyte atoms available for ionization contribute to significant signal enhancement of P, As and Se.

Keywords: ICP-MS, matrix effect, non, spectral interference, carbon

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MP-2 Advantages of sophisticated sample introduction accessories for the trace element analysis of wear metals in organic sample matrices by ICP-OES

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Organic samples require special attention during sample preparation and for introduction into the plasma. Especially the analysis of wear metals in engine coolants and lubricating oils can give inaccurate results if samples are not prepared correctly.

The analysis of wear metals, additives and contaminants in engine fluids such as lubricating oils, hydraulic or coolant liquids provides valuable information to determine the status of the machinery. Wear metal analysis helps to avoid costly damage and extensive down-time of high value engines, generators, gears and other important equipment. Monitoring of specific analytes indicates the health status of the system allowing for preventive maintenance to be appropriately scheduled. Once the engine liquid has been sampled, analysis by ICP-OES is very useful for aiding with maintenance scheduling, basing decisions on the results of analysis. ICP-OES is an ideal technique due to its high temperature source which dissociates any organometallic compounds such as zinc dialkyldithio-phosphates, an additive used as anti-wear in motor oil, and also has the ability to handle difficult organic solvent matrices. This allows the oil or coolant to be directly aspirated into the instrument after a simple dilution, negating the need for any time consuming sample preparation like acid digestion and consequently enabling faster turnaround times.

This poster demonstrates the best practices and advantages of elaborate sample introduction accessories during engine fluid analysis with ICP-OES. Since time is a key factor in preventive maintenance and reducing down-time, a robust and high throughput method is presented in this work.

Keywords: ICP-OES, sample introduction accessories, oils, wear metals, stirring autosampler

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MP-3 Capabilities and performance of quadrupole based LA-ICP-MS

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For the past three decades, ICP-MS has proven to be one of the most versatile and powerful technologies for the analysis of trace metals in a wide variety of samples. This includes samples of different phases, provided they are converted to a vapor or aerosol. For solid samples, this can be achieved using a laser ablation system.

Laser ablation technology has been developed for the past two decades to the point where robust, reliable and easy to use systems are readily available. The complexity of laser ablation sampling has been reduced, with integrated control over the entire analytical system – truly hyphenated LA-ICP-MS. Laser ablation also continues to develop as a technique to enable better spatial resolution with lower analysis times, enabling new applications such as visualization of trace element distributions within a sample.

The nature of solid samples means matrices are always complex and interferences are likely. The development of collision/reaction cell (CRC) technology for polyatomic interference removal has vastly improved data quality; however, CRCs cannot deal with isobaric interferences.

The introduction of triple quadrupole ICP-MS in recent years has opened the door to a new level of interference removal and therefore expanded the capabilities of ICP-MS as a technique. The addition of a pre-filtering quadrupole allows reactive chemistry to be used in the CRC to remove interferences from the analyte signal without unwanted side reactions.

In this presentation, the applicability of laser ablation ICP-MS to routine and research applications will be described. Results will be presented from the analysis of trace metal impurities in bulk products, age determination of accessory minerals, isotope ratio measurements using triple quadrupole interference reduction and finally visualization of elemental distributions within various samples.

Keywords: triple quadrupole ICP-MS, laser ablation, bioimaging, geochronology, bulk analysis

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MP-4 Ultra trace analysis of noble metals in rock samples using triple quadrupole ICP-MS

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The analysis of noble metals, such as the platinum group elements or gold, in geological samples is important to correctly evaluate the content of those metals in an ore, in order to decide whether it is worthwhile to be exploited. Considering the high cost of ore exploitation, it is mandatory to evaluate the concentration in the ore as precisely as possible. However, typically geological samples lead to a complex set of spectral interferences (both polyatomic as well as isobaric), which may severely affect the detection of PGMs such as Rh, Ru, Ir, Pt or Au. Triple quadrupole ICP-MS offers new ways of eliminating these interferences effectively using different reactive gases and a mass filtration step prior to the collision/reaction cell system.

In this study, a certified reference material containing Granodiorite, Silver Plume (GSP-2), which contains many challenging interfering elements for the noble metals such as Hf, Nb, or Sr was used to develop a sensitive and specific method for PGM analysis. Several digested samples of GSP-2 were spiked with Au, Pd, Ir, and Pt at relevant levels and then subsequently analyzed on a triple quadrupole ICP-MS. Different reaction modes were used to determine the best approach to obtaining interference free detection, sub $ng \cdot L^{-1}$ detection limits as well as quantitative spike recovery.

In a second step, another reference material (AMIS 0416, a platinum ore), containing certified levels of PGMs, was analyzed to prove the accuracy of the method. The results indicated excellent recovery despite the challenging sample matrix.

Keywords: triple quadrupole ICP-MS, platinum group metals, PGE, noble metals, ultra trace

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MP-5 Multielement analysis of coolant and antifreeze products using ICP-OES

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The analysis of trace metals in used coolant samples by ICP-OES is a powerful technique used to assess the performance of cooling systems to allow scheduling of preventive maintenance. It is applicable to any closed loop cooling system, but is primarily applied to diesel and gasoline engines since these are more vulnerable to damage from a poorly operating cooling system. The longevity of liquid cooled transmission and hydraulic system components used in industrial production lines are also dependent on a properly operating cooling system. Overheating, due to a failure in the cooling system, reduces oil based lubrication potentially damaging any oil wetted components. Overheating can also contribute to corrosion of components, leading to eventual system failure.

Evaluation of new coolant and antifreeze materials indicates that corrosion protection and solution integrity are strongly dependent on the concentrations of various components. For example, inorganic salts (*e.g.* silicates, borates, phosphates and molybdates), used as corrosion inhibitors, require accurate quantitation as part of the development process of coolant formulations.

This presentation will show how ICP-OES can be utilized for the routine multielement analysis of glycol matrix samples used in coolant and antifreeze products.

Keywords: glycol, antifreeze, ICP-OES, coolant

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MP-6 Simultaneous quantification od iodine and other elements relevant for high level nuclear waste under acidic conditions via ICP-MS for determination of sorption isotherms on Ca-bentonite

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Nowadays, one of the major tasks for humanity is the development of a high level nuclear waste (HLW) disposal in deep geological formations. In order to ensure the compliance with safety standards for more than a hundred thousand years, it is essential to know the important interaction processes between the radioactive waste and the surrounding formations.

Apart from U, Am, Cs and some other elements, especially iodine is a relevant element for nuclear waste repository. ^{131}I is a main fission product of ^{235}U and very hazardous for human beings despite its short half-life ($t_{1/2}$ = 8 d). Small amounts of ^{129}I with long half-life ($t_{1/2}$ = 15.7 Ma) are produced as well. Owing to its high volatility and mobility, which is related to its anionic nature in ground water as iodide, this beta emitter can contaminate for example seafood and milk within a long-ranged area. As a consequence of this, consumption of these products often leads to thyroid cancer.

In order to warrant the safety of a potential HLW disposal site, the retention capability of the environmental geological formations has to be known as well. Clay is one of these considered potential host rocks. Upon its negatively charged surface, typical HLW relevant elements like U, Eu, as homologue of americium and Cs can be immobilized by sorption due to the formation of cationic species, but the retention of iodine by sorption is unlikely. However, there are possible interactions like exchange processes between iodine and some anions, which are part of the clay's structure, that have to be investigated. Not only the interactions between the potential host rock and the elements have to be regarded, the element's influence among each other on retention has to be investigated, too.

Iodine can be quantified for example by neutron activation analysis **[1]** or colorimetric methods **[2]**, but only by inductively coupled plasma mass spectrometry (ICP-MS) a rapid quantification with the other elements in parallel is possible. In this study I, U, Eu and Cs are quantified separate and simultaneously by ICP-MS in complex matrices, for example in solutions with high salinity (up to 5 mol.L^{-1} NaCl) like artificial cement pore water (ACW). Nevertheless, the quantification of iodine is problematic due to the formation of volatile I_2 and HI under acidic conditions which produce an unstable signal and a significant memory effect. In order to avoid the formation of volatile compounds, the speciation of iodine has to be modified. As known from the literature **[3]**, the free anionic I^- can be trapped as a non-volatile NH_4I complex under basic conditions. However, this method suffers from several slightly soluble hydroxide complexes of high valent metals, like Eu, and is not suitable for complex matrices. In this work, iodine will be completely oxidized to iodate by sodium hypochlorite at room temperature **[4]** to enable acidic measurement conditions. The reaction time can be varied from 1 h up to 72 h and samples are at least stable for five days. It is necessary to prepare calibration samples at the same time and with exactly the same reaction time like the samples. The recovery of iodine and the other elements are determined in different media under neutral and alkaline conditions. At last, there is no influence of the oxidation on the recovery of U, Eu and Cs **[5]**.

With this method, sorption isotherms of I, U, Eu and Cs on Ca-bentonite were determined under different conditions. Especially the retention of U and Eu is affected by the presence of each other.

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Keywords: nuclear waste, iodine, simultaneous determination, clay, sodium hypochlorite, ICP-MS

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MP-7 Electrochemistry coupled to flowing atmospheric pressure afterglow mass spectrometry for metabolism studies of polycyclic aromatic hydrocarbons

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The prediction of a drug's metabolism is a crucial factor in drug development. Besides well- established *in vitro* and *in vivo* methods using biological matrices, several biomimetic models have been developed in the past decades. One approach is the application of electrochemistry (EC) for the study of oxidative metabolism reactions. Electrochemistry coupled on-line to mass spectrometry (MS) allows the fast screening of xenobiotics with respect to labile sites in the molecular structure and can mimic the formation of potential metabolites. Conventionally, electrospray ionization (ESI) is used for EC-MS hyphenation, while non-polar substances have been analyzed by means of atmospheric pressure chemical ionization (APCI) in the past **[1]**.

In 2013, Pfeuffer *et al.* introduced a new ADI-MS source called halo-flowing atmospheric pressure afterglow (halo-FAPA) **[2]**. Here, molecules are desorbed/ionized in the afterglow region of a halo-shaped atmospheric pressure glow discharge sustained in helium. Due to the ionization chemistry of halo-FAPA-MS, molecules of a broad range of polarities in the relatively low mass range (*e.g.*, under 1000 Da) can be detected in very low amounts (*ca.* 100 amol). This versatility makes the FAPA ionization source an interesting alternative to standard methods for several hyphenated MS techniques and EC-MS in particular, since the polarity of different xenobiotics and their resulting oxidation products can differ significantly. Nevertheless, only one report on the hyphenation of FAPA and EC-MS exists to date **[3]**.

In this work, an EC-FAPA-MS hyphenation was developed and the scope of this technique was investigated by analyzing the substance class of the polycyclic aromatic hydrocarbons (PAHs), which are of relevance for biomedical and environmental research and have previously been studied via EC-MS with APCI. Mass voltammograms were obtained for a large number of compounds by use of an automated EC-MS setup, where potentials between 0 and 2.5 V *vs* Pd/H_2 were applied to an electrochemical flow-through cell equipped with a boron-doped diamond (BDD) working electrode. The effluent from the cell was fed online into a heated nebulizer and the generated aerosol was ionized by a FAPA ionization source. Generated ions were detected via high resolution mass spectrometry (HRMS) with an orbitrap mass analyzer.

Especially for the highly non-polar PAHs, ionization in the FAPA proved advantageous with respect to sensitivity (*e.g.*, *ca.* 50-fold increased signal intensity for Benzo[a]pyren and its oxidation products compared to APCI). Thus, FAPA ionization proved to be a valuable tool for enhancing the versatility of metabolism studies via EC-MS.

Keywords: electrochemistry, metabolism study, flowing atmospheric pressure afterglow, polycyclic aromatic hydrocarbons

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MP-8 Revolutionizing sample preparation for trace metal analysis with single reaction chamber (SRC) microwave digestion

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A great trace metal analysis starts with a reliable sample preparation. Microwave has been well established as elected technique to efficiently digest organic and inorganic samples. The traditional microwave approach consists in the use of sealed microwave transparent autoclave called rotor-based systems. The main drawback is that they require batching of similar matrices and chemistries because control of the power is based on the reaction of one vessel at a time and the temperature is limited by the material construction of the system. Single reaction chamber (SRC) microwave technology has found a place in a wide variety of market segments, including contract, production and research laboratories in the pharmaceutical, food, agriculture, fossil fuel, petrochemical, polymer, metallurgical, geological, environmental, and consumer products industries, mainly because it overcomes many of the limitations of conventional microwave sample preparation system **[1-5]**. Instead of a rotor with discrete sample vessel, the samples are put into vials with loose-fitting caps, which sit in a rack that is lowered into a larger vessel containing a base load of acidified water. This baseload absorbs the microwave energy and transfers it to the vial, which allows every vial to react independently within the base load and ensures that all samples achieve maximum temperature with pressures contained up to 200 bar. With SRC technology, there is no requirement to batch samples with a similar matrix; so as a result, all sample types can be digested at the same time. Additionally, the high temperature and pressure capabilities of the technology allow even the most difficult organic matrices to be digested in the minimum amount of time. And with the nitrogen-pressurized capping system, samples of widely different analyte concentration can be positioned next to each other in the chamber without concerns of cross-contamination. It is also worth pointing out that there is no minimum volume of acid that must be used with the SRC, which is extremely useful particularly when looking to lower detection capability or to analyzing very small sample sizes. By offering enhanced performance, with high sample throughput, no requirement for vessel assembly and the ability to rapidly cool down, an improved workflow can be achieved without having to batch the samples. SRC technology offers today the capability to process any samples at any time ensuring superior digestion quality.

Keywords: microwave digestion, trace metal analysis, single reaction chamber

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MP-9 Accurate LA-ICP-MS analysis of mineral phases using non-matrix matched reference materials

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The deleterious impact of matrix effects and other elemental fractionation in mineral analysis by LA-ICP-MS is well documented **[1-3]**, yet management of the issues remains an outstanding challenge, especially when high accuracy of the results, approaching that of electron beam-based techniques is required. Use of matrix-matched calibration reference materials (RMs) **[4]** and identical ablation conditions on the RM and unknowns is largely limited to U/Pb dating applications.

Our approach enables analysing different minerals in a single analytical session using a single calibration curve. The approach builds on previous work **[5]** and involves using mineral stoichiometry as a criterium for establishing the appropriate analytical conditions for mineral analysis using non-matrix matched calibration and secondary RMs. Quantification **[6]** is performed using normalisation to a specified total. A single calibration RM is analysed throughout the session under fixed laser conditions, selected to minimise measurement uncertainty. During the same analysis session, secondary RMs are measured using the established laser conditions (*e.g.* beam diameter, fluence, ablation mode: spot or line) required for accurate quantification of the unknowns. Results from the secondary RMs are used for quality control and to estimate separate correction coefficient values for each set of laser conditions required for accurate quantification of the unknowns. Measurement of multiple secondary RMs under the same conditions allows the uncertainty in the correction to be estimated.

When variations in laser parameters on the available secondary RMs and the unknowns are insufficient to achieve accurate results on the unknowns, an additional matrix correction coefficient for each element can be determined and added to the quantification procedure. This coefficient can be quantified once and subsequently reused, provided all analytical conditions remain unchanged between analytical sessions.

We will present the results of LA-ICP-MS analyses of major and trace elements in olivine ($Fe_{0.2}Mg_{1.8}SiO_4$), plagioclase ($Na_{0.4}Ca_{0.6}Al_{1.6}Si_{2.4}O_8$) and ilmenite ($FeTiO_3$) using the above approach.

To facilitate adoption of this protocol, new software has been written for reduction of LA- ICP-MS data. The software package "LADR" (pronounced "ladder") is available for download from the authors' website **[7]** and performs all necessary calculations, including estimation of a "bottom up" **[8]** uncertainty budget.

Keywords: matrix effects, LA-ICP-MS, mineral analysis, data reduction software

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MP-10 Application of a transient ICP-MS measurement for samples with high salinity

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The final storage of high level radioactive waste in deep geological formations is international consensus. Rock salt and clay stone are possible host rocks for a future disposal in Germany. The pore water of clays in Northern Germany shows a strong salinity up to 5 mol.L^{-1} NaCl due to the high presence of rock salt, additionally high concentrations of magnesium and calcium ions are possible, too. In future disposal cement acts as additional barrier to the environment and will be used as stabilisation of the construction. This cement has a great influence on the retaining of the relevant radionuclides in the host rock, mainly, due to a changing of pH in the pore water to alkaline ranges and the leaching of different cations which could directly compete against the radioactive ions.

For safety audits, it is common to realize sorption analysis via batch experiments with clay stone to calculate geochemical parameters like distribution coefficients or Rd-values. After performance of the experiments, the supernatant was analysed with inductively coupled plasma mass spectrometry (ICP-MS). The measurement of samples with a high salt content in the normal ICP-MS is not possible due to the precipitation of salt on cones and the lens system whereby the precision and the sensitivity decrease strongly. Therefore, a high dilution of the samples like 100- or 1000-fold is necessary before ICP-MS measurements. Relevant and interesting elements are europium (homologues of americium), uranium a principal component of the radioactive waste or other fission products like caesium or iodine. For cations under the used conditions, a strong sorption behaviour or precipitation is predicted **[1]**. As consequence, in the supernatant are only low concentrations of the analyte in the range of the limit of determination (LOD) and so a strong dilution for the high salinity is not possible.

In order to solve this problem it is necessary to develop a method, which permits the measurement of low analyte concentrations in presence of a high salt content with the available tools. A method with good potential is a transient ICP-MS measurement. With a modification of the ICP-MS system additional tools like a flow injection system are not necessary. The goal of the modification is to obtain a time resolved signal for the analyte that can be integrated. This peak area should be directly proportional to the analyte concentration. For this reason, the used autosampler ASX-500 (Cetac Company, USA) was externally controlled with the program Hyperterminal which is included in the Windows® (Microsoft Corporation, Redmond, USA) operating system. Additionally, the modified setup allows sample dilution by nitric acid as make up flow via the peristaltic pump of the ICP-MS system **[2]**.

For validation purposes, sorption experiments with europium and uranium (0.04 mmol.L^{-1}) onto Opalinus clay (4 g.L^{-1}) in 10 mmol.L^{-1} sodium perchlorate dissolution were performed. The samples were measured with both methods and the results show only small differences when compared to each other. The application of the transient method to real samples with 1 or 5 mol.L^{-1} ionic strength provides reproducible results.

With this method, sorption experiments onto Opalinus clay with high ionic strength are realizable. To analyse the influence of the hyper-alkaline conditions and the high ionic strength on the retaining, radionuclide concentrations from 5 nmol.L^{-1} to 250 mol.L^{-1} (Cs, Eu, I or U) and different NaCl solutions (0.1; 1; 5 mol.L^{-1}) and an artificial cement pore water at pH 13 were used and compared with results at pH 8. Therefore, a comparable solution to the ACW, a reference pore water with an ionic strength up to 2.5 mol.L^{-1} was used. Europium and uranium show high log Rd values over all used solutions and pH values (8-13) presumably due to a strong precipitation with carbonate and hydroxide in solution. With iodine, nearly no retention was observed. The results of caesium are due to its monovalent characteristics only ascribed with sorption phenomena. The results between pH 8 and 13 in the same solutions show no differences which could result out of precipitation effects. Log Rd values between 1.5 (reference pore water or artificial cement water) and 2.7 (0.1 mol.L^{-1} NaCl) occurred, strong dependently from the injected Cs concentration. With higher initial Cs concentration, the sorption decrease strongly. This effect corresponds to the "Frayed edge sites" which have a high selectivity to cations with low hydration energies like Cs or K, Rb or ammonium but have only a low capacity **[3]**.

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Keywords: new ICP-MS method, time resolved analysis, sorption, clay, nuclear waste

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MP-11 Speciation of phosphorous-based decomposition products in lithium ion battery electrolytes by HPLC- ICP-SF-MS

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The development of lithium ion batteries (LIBs) accompanied the rapid progression of consumer electronics from its beginning in the 1990s. Today, the field of application is still growing, combined with upscaling of LIBs for home storage systems, plug-in hybrid electric vehicles or fully electrified vehicles. The demanding requirements for this application push the development to high capacity and high cell voltage electrode materials, resulting a stronger load and decomposition of the electrolyte **[1]**.

Today, state-of-the-art LIB electrolytes consist of a ternary formulation of 1mol.L^{-1} $LiPF_6$ conducting salt, a linear and a cyclic organic carbonate solvent. Besides a beneficial interphase forming process, starting with the first cycles, the instability of electrolytes show undesired side reactions **[2]**. The assumed equilibrium of $LiPF_6$ and LiF/PF_5 is disrupted by trace amounts of water reacting with PF_5 to highly reactive POF_3 and hydrofluoric acid. After further conversions with water and organic carbonates, the reaction cascade terminates in the formation of organofluorophosphates (OFP) and organophosphates (OP). The structural similarity to chemical warfare agents of OFP aroused interest regarding safety aspects of LIBs **[3]**. This indicates the importance of both, qualitative and quantitative investigations of decomposition products in LIB electrolytes.

High performance liquid chromatography (HPLC) allows the separation of acidic and non- acidic OP/OFP using two orthogonal separation techniques, namely hydrophilic interaction liquid chromatography (HILIC) and RP chromatography. The high structural analogy of these reaction products requires baseline separation for explicit identification as well as for quantification with an ICP-SF-MS.

In this work, speciation analysis of phosphorous-based LIB electrolyte decomposition products was performed with HPLC-ICP-SF-MS hyphenation. Structural information were obtained with HPLC-Ion Trap-Time of Flight-MS. The knowledge of the complexity and quantities of OP/OFP in LIB electrolytes enables the approximation to risk assessments for the recycling of end- of-life LIBs as well as safety assessments concerning abuse and accident cases in home storage or EVs.

Keywords: lithium ion battery, HPLC, ICP-SF-MS, speciation

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MP-12 Development of a microwave-assisted digestion protocol for trace metal analysis in different types of polymers using ICP-MS/MS

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Synthetic polymer particles and fibers < 5 mm, which are either produced in this size range or fragments of formerly larger items, are defined as microplastics (MPs). In the last 15 years, the presence of MPs in the marine and riverine environment raised concern about possible negative effects. Within this context, the hypothesis that MPs serve as a vector for organic and inorganic pollutants into organisms has gained attention.

Many studies have shown that MPs accumulate considerable amounts of persistent organic pollutants in marine environments but only very few studies have focused on the sorption of metals or their species to MPs. Unfortunately, none of these studies indicate a sound methodological validation of the applied methods and procedures, which influences the significance of the available data **[1,2].**

Therefore, the aim was to develop of a fully validated digestion protocol for different polymers, which can be found when analyzing MPs in environmental samples. In particular, a quantitative recovery of the metal content from the different polymer matrices is challenging but mandatory for the accurate quantification by ICP-MS/MS. The developed digestion protocol has been validated using six different plastic CRMs, i.e. ERM-EC680m, ERM-EC681m, NMIJ-CRM- 8123a, NMIJ-CRM-8133a, BAM-H010 and Lead-in-Plastic-QC, and herewith covers the most relevant polymer types (Polyethylene, Polypropylene, Acrylonitrile butadiene styrene and Polyvinyl chloride), which can be found in MP fractions isolated from typical environmental samples such as water or sediment. Besides the certified elements As, Cd, Cr, Hg, Pb, Sb, Sn and Zn, the method was validated for a multitude of other elements.

Two different microwave systems (Discover SP-D and Mars-6, both CEM), different mixtures of nitric acid, hydrochloric acid and hydrogen peroxide, and different temperatures in combination with different hold times were tested for optimization purposes. With the exception of Cr in BAM-H010, the recovery rates of the optimized protocol fell within a range from 94% to 114%. This protocol will be applied to study the sorption of metals to particles of the most common polymer types during incubation experiments using a multi element mix. Sorption isotherms and kinetic profiles will be determined for the relevant metals such as As, Cd, Cr, Hg, Pb, Sb, Sn, Zn etc. Besides to MPs themselves, these metals are partly defined as contaminants in EU directives,
e.g. Marine Strategy Framework Directive and Water Framework Directive.

Keywords: microplastics, acid digestion of plastic, chemical vector, metal sorption

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MP-13 High performance ICP-MS plasma consuming ½ of argon. Standard Fassel torch, robust, high matrix tolerant

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Traditionally ICP-MS instruments with standard Fassel torch **[1]** consume 15-18L.min^{-1} of argon **[2]**. This includes main, auxiliary and injector flows. It is known that the injector flow forms 4-6 mm in diameter analytical channel which is passing through the hot auxiliary plasma. It is logical to expect that all analytical particles must be uniformly heated, atomized and ionized by the auxiliary plasma during the residence time through. This requires that the analytical channel has to be fully submerged into the auxiliary plasma, which has to have large enough cross section (12-15 mm) and uniform properties. This explains why standard Fassel torches (18 mm in diameters) used rather than mini-torches.

Robust plasma, indicated by low CeO/Ce ratio, helps decomposing a sample matrix more completely and is typically achieved at high power of 1.4-1.6 kW. In turns high RF power requires proper torch cooling by argon at about 15-18L.min^{-1}. This is to prevent the torch from melting. It is accepted that higher RF power heats plasma to a higher gas temperature, but what is important to recognize that a low electron temperature is required to reduce the presence of doubly charged species evident by Ba^{2+}/Ba^{+} ratio. This mean that high quality ICP plasma must have sufficiently high gas temperature and sufficiently low electron temperature at the same time. Typically, high plasma oscillating potential is the source of high electron temperature.

It will be presented details of experiments, performance criteria and major considerations of high temperature plasma with unshielded standard Fassel torch consuming only ½ of argon (5-9 L.min^{-1}) and operating within a wide "Hot Plasma" range 0.7 – 1.6 kW power.

Plasma performance has been evaluated on Analytik Jena ICPMS (standard). High gas temperature robustness confirmed by an efficient ionization of high IP elements (Be, As, Se), low oxides CeO/Ce maintained low across a wide power range: 0.7 – 1.6 kW, excellent sensitivity 1 – 2 mln c.s^{-1} per ppb on In and low plasma potential evident by Ba^{2+}/Ba^{+} < 3%.

Reliability and matrix robustness tested with 24% NaCl, 100% Ethanol, 100% IPA solutions.

Keywords: ICP-MS, ICP-MS plasma, torch Fassel, argon, consumption, robust, matrix, temperature, performance, high

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MP-14 Particle analysis of lithium ion battery materials

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The focus of this work is the development of a method for particle analysis of lithium ion battery (LIB) cathode and anode materials by means of inductively coupled plasma based techniques with optical emission spectroscopy (ICP-OES) and mass spectrometry (ICP-MS). Mechanical degradation phenomena arising from the volume change during charging and discharging can severely affect the electrical contact among the particles within the composite material. Furthermore, electrochemically induced particle disintegration at high currents (*e.g.* $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111)) is conceivable to have a major influence on the loss of electrochemical performance.

Based on the fact that the state-of-charge (SOC) of the LIB correlates to the degree of lithiation of the particles, the assessment of electrical contact is accessible by determining the ratio of lithium and host element. For ICP-based techniques, the particle size distribution requires to be narrow and small-sized for the accurate element determination. Furthermore, due to potentially occurring Li^+-H^+ exchange reactions, the sample introduction of NMC cathode materials in aqueous media is not feasible. Therefore, the size dependent separation is performed by the principle of air classification and the particulate sample is introduced by means of an argon flow to the plasma.

The results for the particle classification indicate the applicability for ICP-based particle analysis due to the facilitation of low particle number concentrations and narrow size distributions. The signal ratios for ^7Li to ^{55}Mn as obtained by ICP-MS are characterised by a low relative standard deviation (RSD). In comparison, the RSD for the obtained signal ratios by means of ICP-OES is high. However, the determined signal ratio for NMC532 is in good agreement to the expected ratio based on the results for NMC111 for ICP-OES. Therefore, the results for ICP-MS and -OES exhibit the fundamental functioning for the application in particle analysis.

Keywords: ICP-MS, ICP-OES, single particle analysis, lithium ion battery, cathode, anode

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MP-15 A chemometric approach to access doubly charged and oxide formations and sensitivity for USP < 232> elements on liquid drug samples using aerosol dilution for ICP-MS

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With the recent update of elemental impurities test Chapter <231> from the United States Pharmacopeia (USP) to the Chapters <232,233> , pharmaceutical laboratories are facing new challenges when it comes to elemental quantitation. Working with a myriad of matrices, from raw materials to final drug composition, it is necessary to address the right sample preparation to each group of materials. Some of them, especially liquid drug samples, are potential candidates to dilute- and-shoot approaches, eliminating the sample digestion procedure, which might bring contaminants and errors to the result. New ICP-MS instrumentations can offer several hardware resources to help achieve precise and accurate measurements, such as aerosol dilution prior to introduction into the plasma.

This study aimed to access, with aid of a full factorial 23 design, the behavior of doubly charged ion formation ($^{140}Ce^{2+}/^{140}Ce^{+}$), oxide ion formation ($^{156}CeO^{+}/^{140}Ce^{+}$) and sensitivity (for selected elements of USP <232>) in different liquid drug samples previously diluted with HCl 1% solution and spiked with their respective J values (*i.e.*, the maximum concentration expected considering the maximum daily dose, sample dilution and permissible daily exposure). Variables were gas dilution flow rate (from 0.15 to 0.45 $L.min^{-1}$), collision cell gas He (from 4 to 5 $mL.min^{-1}$) and sample depth (plasma proximity to sample cone, from 7 to 10 mm). Three central points were used to estimate the error, using 95% of confidence interval.

Preliminary results showed that there were interactions between dilution gas flow rate and sample depth that increased doubly charged ion formation, leading to what is believed to be temperature-based phenomena, since less sample is reaching the plasma. Interaction between collision cell gas flow rate and gas dilution flow rate showed the highest increase in doubly charged ion formation, probably due to increase in plasma temperature. As for oxide ion formation, data showed that sample depth and its interactions have no significant effect. Collision gas flow and dilution gas flow are the most important parameters for decreasing $^{156}CeO^{+}/^{140}Ce^{+}$ formation, but no interaction between those variables has been observed. As collision gas flow increases, less polyatomic species achieve the mass spectrometer and detector, hence less signal is observed. In addition, increase in gas dilution flow causes less sample load to the plasma, diminishing the amount of O introduced. Elements that suffers from polyatomic interferences, such as ^{51}V, ^{75}As, ^{52}Cr and ^{78}Se, showed high interactions of collision cell He flow rate and dilution gas flow rate. The combination decreased sensitivity in a rate of 10 to 100 times, depending on the element, when increased (per unit of $mL.min^{-1}$ of He and per unit of $L.min^{-1}$ of dilution gas), as expected, but it minimizes the possibility of interference formation, since less sample is introduced to the plasma. This behavior was different for heavier elements that has less probability of suffering polyatomic interferences, such as Os, Hg and Pb, where only dilution gas flow caused sensibility reduction.

This study has demonstrated that, for different liquid drug samples, the impact of dilution gas is not only related to decreasing sample load to the ICP-MS, but also for minimizing polyatomic interference formation for critical elements such as ^{75}As and ^{52}Cr and less oxide and doubly charged ions formation.

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Keywords: ICP-MS, aerosol dilution, USP <232, 233> , liquid drug samples

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MP-16 Development of an oyster tissue certified reference material for the analysis of total mercury and its use in proficiency testing

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Certified reference materials (CRMs) are an essential part of a quality management system used to establish metrological traceability of measurements results to measurement standards. Mercury is a toxic element of particular concern for the human health and environment. To enhance the reliability of mercury analysis in seafood, an oyster tissue certified reference material (CRM) has been developed at Korea Research Institute of Standards and Science (KRISS). This study thoroughly describes the production of a candidate oyster CRM and its certification by double isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) through a metrologically valid procedure. The developed CRM has been used in a proficiency testing (PT) program organized by the Ministry of Food and Drug Safety (MFDS) of Korea. The use of a metrologically traceable reference value in PT allowed for a reliable evaluation of the performance of participating laboratories.

Keywords: certified reference material, metrological traceability, double isotope dilution, mercury

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MP-17 Barrier Ionization Discharge (BID) detector - A powerful GC detector to quantify permanent gases and light hydrocarbons, evolved from lithium ion batteries

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The interest in lithium ion batteries (LIBs) is still growing as an aspect of energy storage medium for the electro mobility and in stationary implementations. In case of portable electronic devices, LIBs are nowadays the state-of-the-art energy storage technology **[1]**. LIBs consist of a negative carbonaceous anode, a positive lithium transition metal oxide cathode and a liquid electrolyte. The electrolyte is a mixture of different carbonate-based organic solvents, in which the conducting salt is dissolved.

During the formation of the battery cell, an electrolyte decomposition takes place due to reduction at the anode side. During this step, a protective layer - so called solid electrolyte interphase (SEI) - is formed. The SEI protects the electrolyte from further decomposition on the anode side. By-products of the SEI building are different permanent gases and light hydrocarbons **[2]**. Furthermore, gassing as consequence of electrolyte decomposition can occur due to cell failure as well as aging effects and abuse of the LIB cell. Therefore, the qualification and quantification of gaseous products is a safety criterion and of great interest.

Gas chromatography (GC) coupled with various detector systems *e.g.* thermal conductivity detector (TCD) and mass spectrometer (MS) are literature known techniques for characterization. Nevertheless, both detectors suffer from a small linear range for low molecular weight gases especially hydrogen.

As an alternative detector, the barrier ionization discharge (BID) detector can be used. Substances are ionized by a helium-based, dielectric barrier discharge plasma and measured at the collector electrode. This approach leads to a significant improve in the linear range and sensitivity **[3]**.

In this study, the advantages of the BID system for the measurements of permanent gases and light hydrocarbons were pointed out. Furthermore, proof of principle investigations were performed on LIBs after electrolyte decomposition.

Keywords: lithium ion battery, barrier ionization discharge, gas chromatography, electrolyte decomposition

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MP-18 High sensitivity, fast scanning, sector field ICP- MS – Improving sensitivity for laser ablation with the Jet interface

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The long term trend in laser ablation (LA) coupled to inductively coupled plasma mass spectrometry (ICP-MS) has been to: (i) use smaller spot sizes to increase spatial resolution; (ii) investigate elements at lower and lower concentrations; (iii)Improve isotope ratio precision.

In order to achieve all of these aims, the result has been a need to significantly improve the sensitivity of ICP-MS technology. For solution nebulization, it has already been shown that sector field ICP-MS, when utilizing a selected sample and skimmer cone geometry together with a high capacity dry interface pump (Jet Interface), improves sensitivity significantly **[1-3]**.

Here we will demonstrate the sensitivity advantages of sector field ICP-MS with the Jet interface coupled to a modern laser ablation system. We will also show how these sensitivity advantages are bolstered by an extended dynamic range detection system, selectable mass resolution and a high stability magnet and electrostatic analyzer. This enables fast scanning across a wide mass range even if higher mass resolution is required, or if automatic switchovers between counting and analog detection modes are required.

Keywords: sector field, high resolution, Jet interface, laser ablation, sensitivity Improvement, Speed, Fast Scanning

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MP-19 Multi-energy and multi-isotope calibration: strategies for the determination of nutrients and contaminants in meat by ICP-OES and ICP-MS

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Multi-energy $(MEC)_1$ and multi-isotope $(MICal)_2$ calibrations are new alternative matrix matching strategies for overcoming matrix effects during ICP-OES and ICP-MS analysis. They consist of measurement the analyte signal intensity in different wavelengths (MEC) or different isotopes (MICal). In this context, the objective of the current work was to evaluate the applicability of MEC and MICal for determination of the nutrients Ca, Cu, Fe, K, Mg, Na, P, S, Zn , Cr, Mo, and Se and the contaminants Cd, Ni, Pb, and Sr in samples of meat. MEC and MICal were carried out in microwave-assisted acid digested samples of commercial meat and certified reference materials (CRMs) by using only two calibration solutions per sample: S1, composed of 50 % v v-1 sample plus 50 % v v-1 standard solution containing the analytes, and S2, composed of 50 % v v-1 sample plus 50 % v v-1 blank. The S1 and S2 solutions were run separately, and the obtained energy change of various wavelengths (MEC), or isotopes (MICal) were monitoring to build the calibration curves. The methods' accuracy were evaluated by analyzing CRM Bovine Liver and Bovine Muscle (NIST 1577c and 8414) with recoveries in the 81-107% and 89-112% range for the analytes quantified by MEC and MICal, respectively. These results were compared to the classical strategies, as the standard addition (SA), external calibration (EC), and internal standardization (IS). The LOD values were calculated according to IUPAC and, 0.89, 1, 0.17, 0.09, 0.0003, 0.0002, 0.00003, 0.00009, 0.026, 3.46, 0.023, 1, 3.33, 0.54 and 0.46 $g.kg^{-1}$ of dry base were obtained for Ca, Cu, Fe, Mg, K, Na, P, S, Zn, Cd, Cr, Ni, Mo, Pb, Se, and Sr, respectively. Regarding the application, MEC and MICal were performed for quantification of these nutrients and contaminants in samples of commercial chicken, lamb, and beef, and accurate results were obtained for the evaluated samples.

Keywords: matrix effects, strategies calibration, ICP-OES, ICP-MS

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MP-20 Comparison of 193nm and 266nm wavelengths for elemental bio-imaging by laser ablation inductively coupled plasma

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Lasers of deeper wavelengths are well understood to couple with a wider range of materials, particularly transparent materials. This coupling enables a huge range of applications and has been a primary driver of the wide adoption of deep UV wavelengths (specifically 193 nm) for laser ablation systems designed for labs with widely varied applications, particularly labs which analyze materials that are challenging at wavelengths above 193 nm.

It is well documented that elemental bio-images can be generated with 193nm light, but too often the choice of wavelength is based on factors unrelated to wavelength (*e.g.* availability of rep rates, spot sizes at small ranges, long-term laser stability, etc.). By utilzing a 266 nm laser which compares better on these non-wavelength parameters, we are able to examine the choice of wavelenth more directly. As elemental bio-imaging matures as a technique and laser ablation systems are utilized exclusively for bioimaging, the requirement to avoid interaction with the glass substrate makes it necessary to revisit the assumption that 193nm is the ideal laser source systems dedicated to bioimaging.

The ideal wavelength for bioimaging will provide more usable fluences that ablate the sample but not the glass slide holding the tissue. We compare ablations of tissue and glass created with a 193 nm laser (Coherent Existar) in a NWR193 and a 266 nm laser (Polaris 300) in an NWRimage. We posit that the same difficulty with transparent materials that drove geologic users away from 266 nm wavelengths becomes an advantage for elemental bioimaging users, who can use 266 nm light to ablate their tissue samples while minimizing interaction with the glass slide below.

Keywords: LA-ICP-MS, bi imaging, imaging, laser ablation

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MP-21 Using triple quadrupole ICP-MS in routine analysis of environmental and food samples.

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Following its commercial introduction in the 1980's, ICP-MS revolutionised trace elemental analysis by providing fast, multi-element detection for a wide range of applications. However, polyatomic interferences arising from recombination of ions derived from the sample components and the plasma gas were found to limit the performance of the instrumentation. Development of collision cell technology for interference removal provided a major improvement, but even this innovation could not fully remove every polyatomic interference on toxic elements such as arsenic, cadmium, mercury or lead. Polyatomic interferences and in particular, doubly charged rare earth ion interferences, can cause significant bias on key elements under regulation. Examples are selenium and again arsenic, which are interfered by the presence of even moderate amounts of rare earth elements.

Nevertheless, today ICP-MS is routinely used for analysis of trace elements in a wide variety of matrices, including environmental samples, such as waters and soils, all kinds of food and consumer products, clinical research specimens, advanced materials and geological, nuclear and semiconductor samples.

With the advent of triple quadrupole ICP-MS, a new level of interference removal has been achieved. The implementation of an additional quadrupole before the collision cell of the instrument allows pre-filtering of the ion beam to selectively transmit only the masses of interest, effectively suppressing side reactions between other elements in the sample and the cell gas. This pre-filtering capability therefore allows selective chemical reactions to be conducted in the cell to enhance polyatomic interference removal and, in many cases, solve the problem of overlap through doubly charged interferences.

Although triple quadrupole ICP-MS is widely recognized as a major step forward for trace elemental analysis, it is not yet generally accepted as an alternative to collision cell based single quadrupole ICP-MS for routine applications. In this presentation, the latest advances in triple quadrupole ICP-MS technology and how these apply to routine analysis will be described. The enhanced performance provided by this technique will also be discussed, with a particular focus on its applicability in routine analysis of environmental and food samples.

Keywords: food, environmental, trace metals, triple quadrupole ICP-MS

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MP-22 Overcoming the challenges in pharmaceutical analyses, with a focus on OTC allergy tablet analysis with ICP-OES

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With the implementation of USP <232>/<233>, the determination of metals in pharmaceutical products by either ICP-MS or ICP-OES is becoming more common. For medications with daily doses of 1 $g.day^{-1}$ or less, ICP-OES is an ideal analytical technique. However, the analysis of pharmaceutical products poses challenges in sample preparation, dealing with interferences, and compliance with 21CFRPart11. This work will explore ways of overcoming these challenges, witha focus on over-the-counter allergy medications.

Keywords: USP , allergy medication, ICP, OES, pharmaceutical

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MP-23 Ultra-high precision with ICP-OES using continuous real-time simultaneous internal standardization

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When performing measurements with ICP-OES, precisions (*i.e.* relative standard deviations, RSDs) of 1-2% are typical. However, applications exist where greater precision is required, such as when verifying the matrix components of a sample. A simple way of achieving high precision measurements is through Continuous real-time simultaneous internal standardization (CRTSIS), where the internal standard is measured at the exact same time as the analyte, which can result in RSDs of 0.1% or less. This work will discuss CRTSIS and show examples of its implementation.

Keywords: precision, internal standardization, matrix components

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MP-24 Comprehensive software for data reduction of LA-ICP-MS data sets

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In addition to solving the basic Longerich equation **[1]**, successful data reduction of LA- ICP-MS data sets requires a comprehensive approach that includes: identification and removal of transient spikes; corrections for interferences; modelling of variations in background intensity; synchronisation with laser firing time; modelling and correction for down hole fractionation; modelling of calibration drift; assessment of secondary standards and correction for matrix effects; addition of unmeasured elements by stoichiometry; quantification to a total concentration; support for mixed quantification types within a data set, including changes to internal standard and calibration SRMs; and most importantly, correct and robust error propagation from all sources of uncertainty.

Here we present an overview of a new software package "LADR" (**L**aser **A**blation **D**ata **R**eduction, pronounced "ladder') designed to perform all of these functions. To assist the user's comprehension of data quality the software displays graphics for visualisation of time-dependent values such as background variation, calibration drift, and downhole fractionation curves. LADR is able to load data files from most commercially available ICP-MS instruments and it can compute results for trace element analysis, ages for U-Pb dating and quantify arbitrarily defined ratios of any two masses.

Interpretation of LA-ICP-MS measurements is improved if the analyst is presented with a comprehensive uncertainty budget. As well as enabling judicious application of the results, an uncertainty budget rapidly guides the analyst in method optimisation and appraisal of external constraints. Recent workers **[2]** have highlighted the need for robust error propagation, which we believe can be met by the "bottom up" approach of the EURACHEM/CITAC-Guide **[3]** as applied to LA-ICP-MS **[4,5]**. Our LADR software accounts for all sources of uncertainty, which are combined and reported to the user in an expandable view. A significant benefit of determining and quantifying all of the factors contributing to the complete uncertainty is the ability to purposefully resolve parts of the budget relating to precision and accuracy components. To facilitate the interpretation of measurement uncertainty, we introduce the concept of *levels* of uncertainty as a useful practical tool to assist the analyst. The levels we define are descriptively named "Signal Error", "Signal and Background-Noise Error", "Within-Run Analytical Precision", "Full Within-Lab Analytical Precision", and "Full Analytical Uncertainty". The software allows the analyst to choose to report uncertainty values appropriate to a specific intra-run, intra-laboratory, or inter-laboratory comparison. The software package LADR is available for download from the authors' website **[6]**.

Keywords: laser ablation, LA-ICP-MS, data reduction, error propagation

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MP-25 Flat capillary solution cathode glow discharge: a useful modification for improved analytical performance and fundamental characterization.

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The use of atmospheric pressure glow discharges to directly sample aqueous solutions to proceed with elemental analysis through optical emission spectroscopy is already a well-known and effective analytical tool. They represent a powerful approach for fieldable and portable devices that justify a further knowledge of their fundamentals as well as the implementation of alternative plasma generation strategies.

One such device is the solution cathode glow discharge (SCGD). Typically, an SCGD is formed using a metallic sharpened electrode and a flowing conductive solution ($mL.min^{-1}$) acting as the cathode through a rounded glass capillary, applying a DC power of 60 W. The result is an optical emission spectrometry (OES) based elemental analysis approach capable of sensitive detection and precise quantification of many elements in the periodic table. The SCGD-OES can be competitive with other more expensive approaches such as the inductively coupled plasma (ICP) with OES detection and can replace it in certain applications, especially if on-line analysis is required.

In this communication, a recently introduced modification for SCGD generation is discussed: the use of flat glass capillary tubing to introduce the sample solution. Two aspects are focused; in the one hand, its analytical performance is presented, comparing the use of different capillary dimensions; on the other hand, fundamental aspects of the SCGD are enlightened through the visualization and analysis of high frame rate videos of the discharge.

Keywords: liquid electrode glow discharge, glow discharge, elemental analysis, miniaturization, on, line analysis

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MP-26 Characterization and evaluation of a surface wave plasma as an ionization source for mass spectrometry

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Atmospheric pressure plasmas are interesting tools as either excitation and/or ionization tools thanks to their low working requirements and proved performance. Examples of this are inductively coupled plasmas, laser induced plasmas or atmospheric pressure glow discharges. In that sense, lots of efforts have gone to develop instrumentation focused on analytical applications based on this kind of technologies. An interesting option to sustain plasmas at atmospheric pressure is the use of microwave power as it allows the use of several kinds of gases and, with the use of different designs, a wide range of attainable powers that can mark the class of information that can be obtained.

In the work, the S-Wave source (Sairem company) is a compact plasma torch designed for applications at atmospheric pressure. The argon plasma is created in a dielectric tube from a microwave solid-state generator (0-200 W, 2.45 GHz), without reflected power. The source allows the creation of an atmospheric plasma jet. Optical emission spatial distribution measurements were performed with an optical spectrometer (HR2000+, Ocean Optics) and with an ICCD camera (PIMAX-2K-RB, Pearson Instruments). These measurements were realized in free jet conditions to observe the spatial distributions of the main species emissions (argon and ambient air components). The presence of the ions created by the jet were investigated with a time-of-flight mass spectrometer (API-TOF-MS, Tofwerk).

From an analytical point of view, three experimental set-ups to analyze different kind of samples have been evaluated, all of them using a common ionization source based on a surfatron microwave powered plasma and a time-of-flight mass spectrometer. The objective of the project is to develop a set-up capable of multiple kinds of analysis (molecular and elemental information) of different kind of samples.

The first set-up can be described as an ambient desorption/ionization experiment, where the target samples are barely touched before analysis. The second set-up targets the analysis of volatile samples introducing the sample in the most outer part of the plasma plume. The last set-up consisted on introducing either gaseous or aerosolized liquid samples directly through the plasma channel.

Keywords: microwave plasma, ambient desorption, ionization mass spectrometry, mass spectrometry

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MP-27 Quantitative and qualitative analysis of liquid samples by spatial heterodyne Raman spectroscopy

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Spatial heterodyne spectroscopy (SHS) is an optical setup that combines both dispersive and interference based methods to obtain spectroscopic information. It has the high light throughput characteristic for interference based methods, but at the same time it has the high resolution typical of grated spectrometers. The basic SHS optical setup is similar to that of the Michelson interferometer, with the mirrors replaced by diffraction gratings positioned at fixed, equal distances from the beamsplitter and are slightly tilted. The resulting interference pattern is recorded by a digital camera and the spectrum is recovered by using Fourier transformation. Although initially SHS was developed for astronomical and satellite-based atmospheric measurements, where spectroscopy of faint but large light sources is investigated, but in recent years the application of SHS spectroscopy is gaining popularity **[1-3]**.

Our research group is active both in Raman-SHS and LIBS-SHS, due to the fact that there are many overlapping challenges for the two spectroscopies in terms of optical and optoelectronic optimization. In the present study, we investigated the possibility of using SH detection for the qualitative and quantitative Raman spectroscopy of liquid samples. We constructed our own compact spatial heterodyne spectrometer using 300 mm^{-1} gratings (Newport), a 50:50 cube beamsplitter (Thorlabs), dichroic mirrors, bandpass and notch filters (Semrock), a Tamron telelens and a Retiga R1 CCD camera. A DPSS laser (532 nm, 20 ns) with variable energy and repetition rate (up to 100 J and 80 kHz) was used for excitation, with its beam driven through a 10x microscope objective (Thorlabs) to focus the laser light inside the liquid samples. The evaluation of the recorded interference patterns was carried out by self-developed software written in Octave.

In the qualitative experiments, we investigated several oils and additives and employed principal component analysis (PCA) for their classification. It was found that the recorded spectra could be separated well in the subspace of just two principal components. The quantitative experiments were conducted with two sets of binary solvent mixtures (isopropanol-cyclohexane, glycerol-water). The simple univariate method based on the net intensity of one spectral peak did not give good results, but principal component regression (PCR) gave rise to fairly good and robust calibrations.

Our results therefore show that a relatively simple and robust SHS setup can be advantageously used for both quantitative and qualitative Raman spectroscopy.

Keywords: spatial heterodyne spectoscopy, Raman spectroscopy, qualitative analysis, quantitative analysis

Acknowledgments

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MP-28 A novel calibration strategy for the accurate quantification of elemental species using HPLC-ICP-MS

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High performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS) has been demonstrated to be the most commonly used tool for inorganic speciation analysis. Usually, species quantification is performed by external calibration based on peak areas. However, signal drift and matrix effects can adversely affect the accuracy of the speciation data. Corrections by post-column internal standardisation, either continuously or discretely through injection valve, can compensate for moderate signal drift **[1]** but yet sample dependent on-column analyte losses cannot be excluded. When chromatographic separation is combined with calibration by species-specific isotope dilution mass spectrometry (SS-IDMS), these problems can be accounted for and results with high accuracy and relatively low measurement uncertainty can be obtained. However, in many cases SS-IDMS calibration is either not applicable (*e.g.* for monoisotopic elements) or economically not feasible (*e.g.* limited by the cost of the enriched species).

The work presented here demonstrates the potential of a novel on column species-specific internal calibration approach, which offers many of the advantages of SS-IDMS including compensation for on-column analyte losses and signal drift. A significant advantage of the proposed approach is that it can be used with any detector, capable of recording time-resolved data. The feasibility of this novel calibration strategy for accurate quantitative elemental speciation in complex matrices will be demonstrated through the analysis of inorganic arsenic in rice extracts. Accurate speciation results were obtained in scenarios where signal drifts of approximately 20% occurred within a batch of analysis. Both white and brown rice CRMs and i-As spiked rice extracts have been analysed with this method. In all cases, recoveries exceeding 97% were obtained between the certified (or spiked) i-As concentration and the experimentally obtained ones. The method is currently used for the certification of i-As in baby food to support the Commission Regulation (EU) 2015/1006 as regards to the maximum levels of inorganic arsenic in foodstuffs **[2]**.

Keywords: calibration, speciation, accurate, HPLP-ICP-MS, arsenic, rice

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MP-29 Improving laboratory efficiency with a combined prepFAST and chromatography method for chromium speciation

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The determination of Cr, especially the species Cr(III) and Cr(VI), in a variety of different matrices is a widely demanded analysis in many environmental laboratories today. Chromium exists in two oxidation states, a trivalent chromium (Cr(III)) which is essential in carbohydrate metabolism and hexavalent chromium (Cr(VI)) which exhibits highly genotoxic effects even at relatively low concentration levels. Typically labs only test for total Cr, however this is not enough to assess potential toxicity of a sample. Instead measuring for Cr(III) and Cr(VI) provides a more comprehensive measurement.

The prepFAST IC is a syringe driven liquid chromatography (LC) system that can be connected to any ICP-MS and is capable of inline dilution for calibration and sample preparation. The advantage of this system is that it can automatically switch between a direct metal analysis and speciation, which vastly increases the utilization rate of the ICP-MS. Furthermore, the system ensures increased stability of the species due to inline preparation prior to injection. This paper will focus on the validation and implementation of combining chromium speciation in water matrices and total metal analysis of 65 elements in soils and sediments digested with aqua regia using a single automated platform.

Keywords: chromium speciation, LC-ICP-MS, inline dilutions, environmental samples

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MP-30 Inline sample preparation system for micro volume clinical samples

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Clinical laboratories all over the world analyze human blood, serum, and urine to measure for elements that can be either essential for everyday life or harmful to human health. Blood analyses will typically involve some or all of these elements: chromium, manganese, arsenic, selenium, cadmium, mercury, thallium, and lead. Cadmium, lead, and mercury are toxic to humans with no essential role in the human body, whereas chromium, manganese, and selenium play an essential role in the human body as long as the levels are not in excess. The most common way for monitoring elements in blood, serum, or urine is by inductively coupled plasma mass spectrometry (ICP-MS). However, laborious sample preparation steps are normally taken to prepare the samples for analysis by ICP-MS. In the case of whole blood, the samples are generally in small volumes since they are obtained by invasive techniques. Here we will present an inline dilution sample preparation technique for small volumes of undiluted whole blood. The samples will be diluted inline to the ICP-MS, eliminating the sample preparation step. This method will also reduce the amount of consumables (pipette tips, vials, and/or diluent) needed, resulting in a lower cost to operate method.

Keywords: undiluted blood samples, inline sample preparation, ICP-MS, clinical

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MP-31 Automated laser ablation sampling for food safety

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Laser ablation has become an excellent alternative for solid sampling as compared to the laborious sample digestion techniques that are typically required to get all elements into solution for analysis. When combined with inductively coupled plasma mass spectrometry (ICP-MS), LA-ICP- MS is far more sensitive than some of the traditional techniques such as XRF or spark-OES. While many advances have been made to understand laser material interactions, improve high resolution imaging and improve the particle introduction into the ICP, very little work has focused on the automation side. A laser ablation autosampler has been the one key component missing for high- throughput industrial scale applications. Elemental Scientific Lasers has developed and implemented a high-throughput, fully automated laser ablation setup that allows hundreds to thousands of samples to be analyzed unattended. The NWRauto system utilizes the SelfSeal technology, which is a state of the art laser ablation micro-chamber, in combination with a customized carousel and robotic arm. To explore the advantage of such a system, food standards and samples were pressed into pellets and analyzed using the NWRauto in combination with a Thermo iCAP Q ICP-MS. This presentation will look at the important aspects of the hardware as well as the analytical performance for nutritional and/or harmful elements present in food.

Keywords: food safety, LA-ICP-MS, laser ablation automation

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MP-32 Advantages of inline dilution for LC-ICP-MS based applications involving arsenic speciation

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Depending on the species present, the influence of a metal ion or metal complex within an environment or biological system can be essential or toxic. It is well established that methods exist in the literature on how to differentiate and detect essential and toxic species. Typically, a gas chromatography (GC) or liquid chromatography (LC) system is coupled to an inductively coupled plasma mass spectrometry (ICP-MS) instrument. While these instruments continue to improve, there is still one major issue that continues to be debated: Is the integrity of the sample maintained from sample preparation to final analysis?. The following presentation will look at advantages for using inline dilutions to preserve samples for both metal speciation and total metals analysis using Elemental Scientific's prepFAST IC. This is a novel instrument that combines total metals analysis and chromatography into one single, automated platform combined with ICP-OES or ICP-MS. The applications discussed will include arsenic speciation in urine and a combined total metals (essential and toxic elements)/arsenic speciation in apple juice.

Keywords: arsenic speciation, clinical, food, chromatography, ICP-MS

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MP-33 High-performance LA-ICP-TOF-MS imaging combining the Cobalt LA cell and icpTOF

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Laser ablation ICP elemental imaging has progressed from slow acquisition and cumbersome assembly of images in post-processing towards a real 2D imaging methodology that is easy to use. The main limiting factors that define the forefront of current innovation are the wash- out time of the LA cell, the measurement time on the mass spectrometer, and speed of data (post)processing.

Here, we will focus on current hardware capabilities of a new laser ablation cell (Teledyne CETAC Cobalt) coupled to an ICP time-of-flight mass spectrometer (icpTOF, TOFWERK AG).

The cobalt cell allows full signal wash-out and resolution of individual laser pulses at repetition rates of well over 100 Hz. The fast sample aerosol transport also causes an increase in sample-to-background signal, and thus in sensitivity.

Sequential mass spectrometers do not allow measurements of more than one or a very few isotopes within the 2-4 ms a single pulse signal response lasts, which would limit imaging applications to these few analytes.

This acquisition speed bottleneck is overcome by utilizing the icpTOF. This instrument acquires the full mass spectrum at a rate of several tens of kHz, enabling full elemental information from every single laser shot. Therefore, one laser pulse per pixel is sufficient, drastically shortening the acquisition time for a given image. Full coordination information is saved with every measurement, which allows for a real-time preview and straight-forward image creation in post- processing.

We present examples of geological and biological applications, as well as performance metrics measured on standard materials, demonstrating a total ionisation efficiency and limits of detection comparable to, and isotopic ratio precision exceeding results achievable on *e.g.* quadrupole ICP-MS instruments.

Keywords: LA-ICP-TOF-MS, time, of flight, laser ablation, imaging

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MP-34 Using multi-lines post-analysis data processing for the enhancement of ICP-OES performances

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Today, detection systems in ICP-OES are essentially based on charge transfer device detectors allowing the acquisition of a large part of the Ultra-Violet-Visible (UV-Vis) spectrum simultaneously. The amount of information available for each element is therefore huge and easy to obtain. However, in order to benefit from all of it, adequate data processing relying on a robust mathematical approach has to be developed. This study presents the "Total Sum model" multi-lines post-analysis data processing based on the "excess variance" weighted mean approach. The results, obtained from the use of the multi-elemental certified reference material "CETAMA EQRAIN 22", show a decrease by a factor till 4 both for the measurement uncertainty and the detection limit, when using the "Total Sum model" instead of using the result of a single emission line. Results obtained for iron, arsenic and palladium analysis in "CETAMA EQRAIN 22" CRM are presented and discussed.

Keywords: ICP-OES, weighted mean, multi, line analysis

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MP-35 Space charge effect behind hyperskimmer in ICP-MS

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Due to a large ion flux in ICP-MS, the space charge effect on the ion transmission and the characteristics of the mass spectrometer is significant. It may sufficiently contribute to matrix effects and mass bias. The deviation from plasma charge neutrality occurs shortly after expansion through hyperskimmer. The electrons diffuse to the inner surface of the hyperskimmer. The uncompensated positively charged ion beam continues to move forward. The region behind the hyperskimmer is subject to dense charge and the most pronounced space charge effect. The investigation of the space charge effect in this region is presented in this work.

The numerical simulation is done using commercially available program SIMION. The measurements of the radial profile of Ba ion beam were conducted using the LIF technique. The total ion current were measured at a metal plate behind the hyperskimmer as a Faraday plate.

The transmission of analyte ions with different masses through the hyperskimmer in the presence of space charge is studied. The investigation takes into the account of electrons and bulk argon ions. The total ion current is found experimentally and is compared to simulation for space charge effect. The simulated ion beam extension due to space charge is in agreement with what is measured experimentally using LIF technique. It is found that the heavy ions are transmitted more than light ions into the mass spectrometer. The degree of transmission, depending on mass, is obtained quantitatively.

Keywords: interface, hyperskimmer, numerical simulations, SIMION, ion beam, space charge

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MP-36 Recent advances in detection, quantification and population distribution of single and dual analytes in single cell and single particle ICP-MS

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Single Particle (SP) and Single Cell (SC) -inductively coupled plasma mass spectrometry (- ICP-MS) is based on quadrupole mass filters and involves microsecond dwell times (typically < 100 s) and *continuous* data acquisition (*i.e.,* no settling time). This allows for multiple intensity data points to be acquired during a single nanoparticle event (typically 300-500 µs long), leading to a precise definition of the nanoparticle transient signal. The flexibility of the peak detection algorithms used in both the SP- and SC-ICP-MS software applications is also crucial in detecting small event signals close to the detection limits of the system while not sacrificing the detectability of large nanoparticles at the high end and hence preserving the dynamic range of the system in terms of event intensity.

Measuring more than one element in the same event would allow naturally occurring nanoparticles to be distinguished from their engineered, alloyed (core-shell) counterparts, or the comparison of a nutrient metal and uptake of a different metal into cells. The sequential nature of quadrupole-based systems poses a challenge considering the relatively short transient events associated with nanoparticle signals and the fact that the speed of peak hopping is limited by the ion travel time through the quadrupole mass analyzer.

Here we will demonstrate how the *fast-scanning* SP- and SC-ICP-MS techniques can be adapted to obtain both qualitative and quantitative information on dual analyte analysis. We will show results on both SC- and SP-ICP-MS to quantify size and population composition within the suspensions using mixed suspensions of Au, Ag and AuAg (core/shell) NPs for SP-ICP-MS and mixed solutions of micron beads containing either just Eu or Eu and Lu for SC-CIP-MS.

Keywords: single particle, single cell, ICP-MS

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MP-37 Applications of dual analyte analysis of metals in single particle and single cell ICP-MS

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Single particle (SP)-ICP-MS has become a staple for nanoparticle (NP) analysis for measuring particle size, particle concentration and particle transformations, such as aggregation and dissolution. More recently single cell (SC)-ICP-MS has been developed on the same concept for quantifying the metal content or metal uptake on an individual cell basis. Although the sample introduction is very different for these two techniques the NP or cell detection is the same with short dwell times and no settling time integral for quantification of the NP size or metal concentration in the cell. However, the interest in being able to quantify two elements in an individual NP or cell has been growing. It will allow for the possibility of determining man made verses natural NPs, or the uptake of a metal into the cell with the corresponding down regulation of a nutrient metal, thus giving a deeper insight in to the world of nanotechnology and cell processes. Here we discuss PerkinElmer's advancement in SP- and SC-ICP-MS to allow for dual analyte analysis and show the first results in both NP and cell analysis achieved with this technique.

Keywords: single particle, single cell, ICP-MS

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MP-38 Application ICP-MS and ICP-OES for measurement of trace elemental impurities and certified target value in CRM

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For metrological assurance of high-precision inductively coupled plasma mass spectrometry and optical emission spectroscopy, the Russian Metrological Institute of Technical Physics and Radio Engineering began to develop reference materials of the metals mass fraction in solution, designed especially for methods with inductively coupled plasma (ICP CRM). The ICP CRM is represented by solution with certified value of target analyte mass fraction. The ICP CRM is packed in HDPE bottles with the capacity of 30, 60 or 125 cm^3. Gravimetric preparation is a practical realization of mass fraction units. The value from the gravimetric preparation is used as a certified value of the reference material. ICP-MS and ICP-OES are used to confirm the certified value of the reference material.

Keywords: inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy, water, aqueous solution, reference material

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MP-39 The effect of instrument sensitivity on sample throughput

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The number of samples which can be analyzed within a given time interval is an important characteristics of every analytical instrument. Mainly, there are three factors influencing that speed of analysis: transfer time, dwell time, and washout time.

The study presented here is about dwell time of MS instruments. Its contribution to the total cycle time and the optimization potential therein is discussed. We demonstrate that instrument sensitivity is not only influencing the limits of detection but also sample throughput. This can be achieved by a considerable shortening of the dwell times if the sensitivity is high.

We compare measurements using identical setups of mass spectrometers which differ in instrument sensitivity only. We demonstrate how sensitivity gain is converted into dwell time reduction. As a boundary condition, the relative error of all measurements was monitored in all experiments. For direct comparisons, it was kept constant.

For a mass spectrometer with the average sensitivity 10 times higher than a standard MS the dwell times can be reduced by a factor 6 without losing accuracy. Considering the complete measuring cycle this speedup is diluted, however. In total it allows 3 times more samples per time interval to be analyzed.

Keywords: ICP-MS, sensitivity, dwell time, throughput

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MP-40 Determination of nanoparticles using ICP-MS

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The determination of nanoparticles using ICP mass spectroscopy is based on intensity bursts produced by these particles exceeding the continuous intensity level. Several mathematical algorithms have been suggested to deduce the nanoparticle properties from time-resolved intensity measurements. Within this study, we investigate the influence of boundary conditions onto the results of those computations.

Initial calibration measurements are required to deduce key parameters for nanoparticle computation. We show which derived properties are sensitive to selected boundary conditions and which are less. This allows for a skilled prediction of the error intervals for the nanoparticle properties. Moreover, this leads to recommendations for the setting of boundary conditions where possible.

This work is based on measurements with the PlasmaQuantMS® mass spectrometer. The data obtained were cross checked to the properties of reference materials.

Keywords: ICP-MS, nanoparticles, algorithm, data analysis

α - Presenting author

MP-41 Improvements in the determination of uncertainties of isotopic ratios for uranium samples thanks to IAEA Round Robin

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In the field of nuclear energy, the role of analytical chemistry is growing thanks to an increasingly widespread usage of powerful instruments. Among analytical instruments, ICP-MS equipped with multiple collectors (MC-ICP-MS) allows measurements of isotopic composition of various elements, with a very low uncertainty. During MC-ICP-MS measurements, all ion currents are biased by mass discrimination and other effects (detector gain, abundance sensitivity background, dead time...). So, various corrections must be applied to all measurements to determine accurate and precise isotope ratios. The use of certified isotopic reference materials (IRMs) associated to a sample standard bracketing (SSB) method allows us to determine accurate isotope ratios. The ratios are determined taking into account in particular the mass discrimination, the uranium hydride ions, blanks and isotopic reference materials measurements. The uncertainties associated to those ratios are then calculated.

For example, in the case of uranium, atom ratio of ^{235}U to ^{238}U is measured with a relative uncertainty better than 0.1%. For the ^{234}U and ^{236}U isotopes, the uncertainties associated to the atom ratios of ^{234}U to ^{238}U and ^{236}U to ^{238}U are greater due to the lowest abundances of those isotopes. The performance of the laboratory to determine uranium isotope ratios and the uncertainties associated is evaluated by participating to inter-laboratory tests.

The nuclear material Round Robin proficiency testing scheme (NM RORO), organized by the International Atomic Energy Agency (IAEA) is a reliable and objective tool for assessing and monitoring analytical performance of laboratories in the area of nuclear material analysis. We have participated to three consecutive NM RORO (2015, 2017 and 2019). These RORO allow us to testify the accuracy of the SSB method to determine uranium isotope ratios. Concerning the calculation of the uncertainties, the 2015 NM RORO helped to improve the determination of the uncertainty associated to the $^{236}U/^{238}U$ ratio (which was beyond-acceptable-range zeta-score). The 2017 NM RORO lead to good results for the determination of uranium ratios and their associated uncertainties and allows us to validate our method.

Keywords: uranium, MC-ICP-MS, uncertainty

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MP-42 Solving doubly charged ion interferences using ICP-MS/MS with nitrous oxide

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Collision/reaction cells (CRCs) have greatly improved the accuracy of ICP-MS by controlling spectral interferences. Nowadays, helium (He) collision cell mode is widely used for the trace element analysis of environmental and food samples. It is especially effective at resolving spectral interferences that arise from overlapping matrix or plasma-based ions. He mode uses kinetic energy discrimination (KED) to reduce the transmission of all common matrix-based polyatomic interferences under a single set of cell conditions. However, a different approach is needed to remove doubly charged ion interferences (M^{2+}), since He mode enhancesthe interference. A solution is to use N_2O as a reaction cell gas in the CRC. Since not all elements suffer from doubly charged ion interferences, most elements can be analyzed using He mode. The remaining elements can be measured in reaction gas mode. N_2O resolves the doubly charged ion interferences via O-atom transfer. Oxygen (O_2) can also be used as the cell gas, but N_2O provides the following advantages: (i) the O-atom transfer method with N_2O is effective for more elements than O_2. The graph shows the O-atom affinity of elemental ions with that of an O atom and N_2; (ii) higher sensitivity for selenium (Se) – an important element in many applications – because the O-atom transfer of Se^+ with N_2O is exothermic; (iii) no formation of MO^{2+} from the reaction with N_2O. Some M^{++} reacts with O_2 to form MO^{2+} causing overlaps on analyte ions.

Details of the reaction gas cell method, test results and figures of merit will be provided.

Keywords: ICP-MS/MS, doubly charged ion, interference, nitrous oxide

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MP-43 Uses of Agilent 8900 ICP-MS/MS for nuclear applications.

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Thanks to its high sensitivity and capability to differentiate the isotopes of an element, ICP- MS has become a powerful tool in the nuclear industry and for radioactivity studies. However, some analytical challenges cannot be solved by Single Quadrupole or High Resolution ICP-MS systems.

Some of the challenges can be solved using Agilent 8900 ICP-MS/MS. Controlled reactions can be performed in the reaction cell using the MS/MS mode and in addition, MS/MS configuration with 2 quadrupoles operating with a 1 amu mass resolution provides excellent abundance sensitivity.

Using those features, uranium isotopic ratios can be measured free of UH^+ interferences using reaction with oxygen in the reaction cell in MS/MS mode. Radionuclides such as Neptunium and Plutonium could be measured in a uranium matrix by avoiding the peak tailing from the matrix. The perfect control over the masses entering and exiting the cell enables the removal of isobaric interferences that are usually handled through long and complex sample preparations. The example of the measurement of Strontium 90 free of Zirconium 90 will be developed.

Keywords: ICP, MS/MS, 8900, Nuclear, interferences

α - Presenting author

MP-44 Improvement of the nanoparticle size limit of detection for SP-ICP-MS using a desolvating nebuliser and peak detection algorithm optimisation to distinguish small particles from ionic background with the HR-ICP-MS Attom

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A Engineered nanoparticles are regularly being used in in a multitude of industrial products. The release of these substances into the environment and the questions raised about a potential harm for the human health require the development of methodologies to characterise those materials over the range of anticipated sizes and concentrations present in-situ. SP-ICP-MS has been proven in recent years to be a useful tool for particle counting, sizing and quantification. The HR-ICP-MS Attom allows the acquisition of data with a dwell time down to 10 µs, (with no settling time). The combination of fast signal acquisition capacity and high sensitivity make the Attom a promising instrument for this technique. In this work, the capability of this instrument demonstrates the further improved limit of detection achievable with the use of a desolvating nebuliser.

Due to its high ion transmission efficiency, the AttoM already reaches low limits of detection for SP-ICP-MS in conventional nebuliser and spraychamber introduction mode (6 nm for Au, Ag, CeO). In this work, the use of a desolvating nebuliser improves these limits of detection further (4 nm for Au, Ag, CeO).

The detection of smaller nanoparticles is degraded by the presence of ionic background signals and the noise on the background signal becomes a significant parameter to consider. The ability to measure at dwell times less than the signal duration of the particle and then subsequent processing of the signal data allows for more accurate distinction of particles from background signals. This work will describe the use of advanced processing methods to reduce false positive detection and improve signal to background noise. Data from a silver nanoparticle dispersion experiment in a lake ecosystem will be used to show the effectiveness of desolvation and the processing methods.

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MP-45 A new approach for effective ionisation of elements with high ionisation potential such as fluorine and oxygen in pulsed glow discharge mass spectrometry with using a neon plasma

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One of the primary directions for the modern analytical scientists is the development of the reliable and accessible methods, applicable for direct analysis of solids (geological materials, crystals *etc.)*, containing elements with high ionisation potential. Recently, there were several studies devoted to the use of GD-MS for the determination of the most challenging high ionisation energy elements, such as F **[1]** and O **[2,3]**. However, there are interferences and not enough intensities of fluorine and oxygen in the argon plasma. To solve these problems, it was suggested to use the neon as a discharge gas.

In this study, the more effective mechanism of fluorine and oxygen ionization has been determined. The processes in neon plasma have been studied. It was expected that the use of neon as plasma gas may be beneficial for fluorine and oxygen quantification in Penning ionisation, because energy of metastable level for neon (16.6 eV) is considerably higher than oxygen ionisation energy (13.62 eV) and comparable to the fluorine ionization energy (17.42 eV). Also, the approach to determination of oxygen and fluorine with using electron ionisation **[1,3]** has been verified in the neon plasma. To solve the problem of oxygen and fluorine quantification, the following parameters were optimised: repelling pulse delay, discharge duration, voltage and pressure in the discharge cell. Relative sensitivity factors were used for quantification; titanium was used for normalisation. Penning ionisation of oxygen in neon plasma was also observed but was found to be less efficient, compared to electron impact ionisation. Overall, the use of neon compared to argon significantly benefited fluorine and oxygen determination; the limits of detection for oxygen (0.0005 mass %) and fluorine (0.0002 mass %) decreased several times as a result of more effective ionisation. The fluorine doped potassium titanyl phosphate (KTP) single crystals and standard geological material were used for analysis. The improvement was especially pronounced for fluorine, due to the alleviation of plasma-based interferences. However, for other KTP constituents – potassium, phosphorus and titanium – the analytical performance was expectedly lower, due to the lower sputtering rates in neon discharge. Thus, the use of neon as a discharge gas for glow discharge mass spectrometry was found to be preferable for the determination of high ionisation energy elements such as oxygen and fluorine.

Keywords: mass spectrometry, pulsed glow discharge, oxygen determination, fluorine determination, neon, direct determination, combined hollow cathode, potassium titanyl phosphate (KTP)

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MP-46 Deciphering the lithium ion movement in lithium ion batteries: determination of the isotopic abundances of ^{6}Li and ^{7}Li

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The growing demands for renewable energies and the urge of reducing the human ecological footprint increases the attention for lithium ion batteries (LIBs) for mobile and stationary use. While being a technology originating from in 1991 by Sony **[1]**, the state-of-the-art LIB uses carbonaceous materials and lithium transition metal oxides ($LiMO_2$; M = Nix, Coy, Mnz (x+y+z=1)) as the negative and positive electrodes, respectively.

One major drawback of this technique is the subsequent capacity loss during operation. The formation in the first cycle and the ongoing growth of the solid electrolyte interphase (SEI) on the anode and the cathode electrolyte interphase (CEI) on the cathode are some of the reasons for these losses. These interphases form on the electrodes due to surface reactions because of reductive/oxidative potentials by decomposition of the electrolyte and therefore consumption of active lithium that cannot be utilized for electrochemical processes **[2]**.

Therefore, plasma-based mass spectrometric techniques are used in this work to analyze different components of LIBs, aged under charge/discharge conditions. In detail, a ^{6}Li-enriched electrolyte was prepared to perform an isotope dilution analysis (IDA). Additionally, the electrodes are measured by inductively coupled plasma-mass spectrometry (ICP-MS) for bulk analysis and glow discharge-sector field-mass spectrometry (GD-SF-MS) for depth-resolved IDA. The electrolyte is analyzed by ICP-MS, as well. These techniques will provide a better understanding of the processes behind the SEI/CEI formation and whether the decomposed lithium originates only from the electrolyte or from the positive electrode, as well.

The cycling experiments are conducted at different charging rates and numbers of cycles for MCMB/NCM622 ($LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$) full cells.

Keywords: glow discharge mass spectrometry, lithium ion battery, lithium ion migration, isotope analysis

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MP-47 Application of glow discharge mass spectrometry for analyzing Si/C-composite anodes for lithium ion batteries – determining the influence of the state of charge and dry film thickness

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The lithium ion battery (LIB) was first commercialized by Sony in 1991 **[1]**. The state-of- the-art technology consists of carbonaceous materials and lithium transition-metal oxides ($LiMO_2$; M = Nix, Coy, Mnz (x+y+z=1)) as the negative and positive electrodes, respectively. While the performance and capabilities of LIBs are growing rapidly, the technology has drawbacks regarding the widespread adaptation and consumer acceptance of electric vehicles (EVs) which is arguably accounted to the limit range due to a modest capacity of batteries of the current generation **[2]**.

Therefore, silicon is a promising contestant as a future anode material with a theoretical capacity of around 3500 $mAh.g^{-1}$ compared to 370 $mAh.g^{-1}$ of commercially available carbonaceous anodes. Unfortunately, this material still has serious problems such as a severe volume expansion (> 300%) during lithium insertion which slows down the commercialization and leads to the use of Si/ C-composite anodes to compensate the drawbacks of both materials **[3]**.

In order to create more sophisticated insights into different influence factors of the charging behavior of these composite electrodes, it is important to use appropriate analytical methods. Therefore, a glow discharge sector field mass spectrometry (GD-SF-MS) method is developed in this work to analyze the homogeneity and content of lithium in Si/C-composite electrodes in different states of charge (SOCs) and with different dry film thicknesses (DFTs) regarding soft conditions with slow sputter-rates for complete depth profiles to receive the highest amount of information possible with this method.

Keywords: glow discharge mass spectrometry, lithium ion battery

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MP-48 Fast analysis of direct injected gaseous samples using radiofrequency pulsed glow discharge time-of- flight mass spectrometry

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Pulsed glow discharge (PGD) is a well know technique traditionally used for the direct analysis of solid samples. The dynamic plasma generated by the PGD sources with different ionization mechanisms along the pulse (*e.g.* prepeak, plateau and afterglow) **[1]** has played a very important role in the development and evolution of glow discharge as reliable and accurate analysis technique even for solid insulating samples.

In the last decades, the research in PGD as analytical tool has advanced a step further with the use of PGD for the ionization, identification and analysis of gaseous compounds. The use of the different pulse regimes with their different ionization mechanisms produced provides the ability to obtain both molecular information and fragments of volatile organic compounds (VOCs). This feature has been demonstrated even for the identification of isomers due to the different ionization energies necessary for different fragments formation (even along the same pulse regime as in the case of the afterglow) **[2]**. In previous works developed in our laboratory, the PGD as an analytical tool has been well demonstrated for the analysis of VOCs in waters and also for the direct analysis of gaseous samples. The development of a new interface, that allows introducing the sample away from the plasma to use a region with a high density of reactive ions, has allowed the analysis of molecules with short fragmentation and detection limits below those established by the European Union in terms of air quality control **[3]**.

In the work presented here, this new innovative interface has been used for the analysis of several VOCs. The ionization produced by the PGD with this sample introduction system has been studied under different plasma conditions for different VOCs. The use of a prior separation technique has been investigated in a preliminary way. In this case, a multicapillary column, that allows the direct injection of larger volumes of gas, has been used and studied for the analysis of VOCs with analytical purposes in relatively complex samples.

Keywords: PGD, VOCs, glow discharge interface, direct analysis

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MP-49 Direct quantification of high-ionisation energy elements by pulsed glow discharge mass spectrometry – a study of different discharge gases

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The quantitative determination of high ionisation energy elements in various natural and technological materials claims high requirement to the analytical techniques employed. Currently, glow discharge mass spectrometry and optical emission spectrometry (GD-MS and GD-OES, respectively) are widely and successfully used for the direct elemental analysis of various conducting and dielectric solids. Recently, there were several studies devoted to the use of GD-MS for the determination of the most challenging high ionisation energy elements, such as F **[1],** O **[2,3]**, Cl **[4]** and N **[5]**.

This study contains comparative consideration of different discharge gases and gas mixtures for pulsed GD-MS in means of their possibilities to provide effective ionisation of non-metals (F, O, Cl and N). Ionisation potentials of these elements are higher than that of argon metastable levels. Therefore, the Penning ionisation, which is a dominating ionisation mechanism in pulsed glow discharge, is ineffective for these elements in the case of conventional argon discharge.

Two approaches were proposed to solve the problem. Firstly, the use of other noble gases with higher energies of metastable levels, such as helium and neon, is considered. The use of pure helium is hardly applicable owing to very low sputtering efficiency related to the low atomic. Therefore, its mixtures with heavier gas as argon or krypton were discussed. Neon was used without additives.

Alternatively, another ionisation mechanism has been tested for argon plasma. High ionisation energy elements were shown to be ionised by the high-energy electron impact, formed on the front of the discharge pulse under short repelling pulse delay. In this case, the ionisation takes place in non-collision zone of the mass spectrometer between sampler and skimmer and thus the recombination does not take place. Argon and argon-hydrogen mixture containing 0.3 % of H_2 were considered.

Thus, different discharge gases and gas mixtures were studied as plasma medium for direct quantification of high ionisation energy elements by pulsed GD-MS. Combined hollow cathode was employed as a discharge cell. Both conductive (steel) and dielectric samples (single crystals of pure and fluorine doped potassium titanyl phosphate and standard geological material SGD-1A) were used for the analysis. The properties of plasma and ionisation processes have been studied. The most effective mechanisms of O, F, Cl and N ionisation were determined. The following discharge parameters were optimised for all discharge gases: repelling pulse delay time, discharge duration, voltage and pressure in the discharge. Relative sensitivity factors were used for quantification. The limits of detections were determined. The ability to quantify other constituent elements of the sample in a single run was also considered.

Keywords: pulsed glow discharge, mass spectrometry, high ionisation energy elements, discharge gas, helium, neon, oxygen, fluorine, nitrogen, chlorine, combined hollow cathode, potassium titanyl phosphate (KTP)

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MP-50 Gallium analysis using s-pulsed fast flow glow discharge mass spectrometry

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Sector field s-pulsed fast flow glow discharge mass spectrometry (s-FF-GD-MS) is routinely applied for the direct analysis of a wide range of materials. Especially for aerospace, electronics and photovoltaic industries, quality control at high sample turnaround is required, for example for nickel super alloys producers or high purity copper refineries.

The Thermo Scientific™ ELEMENT GD™ PLUS GD-MS features a fast flow glow discharge source that can be operated in continuous or pulsed mode. For most metals, including indium and tin with rather low melting points, no special requirements for sample cooling were needed in either operation mode.

Gallium metal samples with a melting point below 30˚C can only been analyzed in pulsed mode, taking advantage of the much lower power requirements compared to DC operation to avoid melting. With the current instrument setup, sample cool down was manual and rather slow, so that sample turnaround was not significantly higher than with previously used cryo cooled GD-MS instrumentation (VG9000).

In order to provide a tool for onsite quality control in Ga industry and for the emerging market of thin film CIGS solar cells, a gallium Kit is developed for the ELEMENT GD™ PLUS GD-MS. This contribution summarizes first results of the workflow solution for a simple and clean sample preparation, providing a faster sample cooling and automatic warm-up after analysis for high sample turnaround times.

Keywords: GD-MS, fast flow, gallium

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MP-51 Analysis of highly boron-doped diamond thin films: comparison of GD-OES, SIMS and Raman spectroscopy

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Depending on its boron impurity concentration diamond can be utilized as either a semiconductor with outstanding electrical properties or as a chemically stable metallic conductor. Therefore, diamond layers prepared by chemical vapor deposition (CVD) have been extensively studied as a promising new material in power electronic or electrochemical applications **[1,2]**. The primary parameter affecting the properties of born doped diamond layers is the boron atom concentration and its depth distribution. Current methods able to measure boron in diamond are limited and their analysis is neither trivial nor straightforward. Methods mentioned in this work are relative, *i.e.*, the measured signals cannot be interpreted by first principles, therefore their interpretation depends on an initial calibration. Sputter rate-corrected calibration **[3]**, using several certified reference materials, other than diamond, with a known composition is used for boron analysis by glow discharge optical emission spectroscopy (GD-OES). Secondary ion mass spectrometry (SIMS) **[3]** relies on a reference sample with a known concentration of boron in a diamond matrix prepared by ion implantation. Raman spectroscopy, although not generally a typical method for analysis of elemental composition, is a non-destructive method of choice in this particular case **[4,5]**, here Raman peaks (inelastically scattered light) depend indirectly on the amount of boron and it is thus desirable to establish experimentally how the Raman signal reflects the boron concentration.

In our experiments, a very good agreement between GD-OES and SIMS results has been obtained for heavily boron doped diamond layers (a good correlation for different boron concentrations and a difference by a factor of 0.82 in absolute terms, i.e. by 20% relative), whilst both methods represented two fundamentally different traceability chains. This suggests that a very reasonable level of accuracy was achieved using these analyses. In this contribution, the GD-OES calibration will be described in detail and examples of depth profiles of boron in typical samples will be given, as well as the relation between boron concentration in the layers and the composition of the reaction gas used in their deposition. Finally, we also demonstrate, based on these results, that the boron concentration can be determined from the analysis of the zone center phonon line in a Raman spectrum.

Keywords: boron, diamond layers, glow discharge optical emission spectroscopy, secondary ion mass spectrometry, Raman spectroscopy

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MP-52 Spatially-resolved glow discharge mass spectrometry analysis

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We discuss the possible use of glow discharge mass spectrometry (GD-MS) for spatially- resolved analyses. In our model, the sample is being moved with respect to a fixed glow discharge source. To achieve this, we use an xyz high-vacuum translation stage with a membrane bellow to allow in situ movement of the sample with respect to the glow discharge source, coupled to a quadrupole mass analyser. This construction allows for elemental mapping through a pixel-by-pixel rastering method.

As a result, we show multi-elemental maps of several model samples like a dot, stripe, concentric circular structures, and other structures. We discuss the resulting lateral resolution parameter in relation to the shape and diameter of a tantalum mask mounted between the sample and the glow discharge anode. Also, we discuss rastering approach parameters, such as step size and translation rate.

The GD-MS spatial resolved maps are created with the use of SMWJ-01 quadrupole mass analyser, equipped with a glow discharge source operating in 0.7Tr argon working gas, DC discharge voltage of 1100V and 1.2mA current.

We also compare the GD-MS maps with secondary ion mass spectrometry (SIMS) images created with Hiden SIMS Workstation using 5keV, O_2^+ primary ion beam.

Keywords: glow discharge mass spectrometry, spatially resolved analysis, lateral resolution, DC glow discharge

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MP-53 Direct analysis of gold and silver nanoparticles of different sizes from dried droplets using substrate- assisted laser desorption single particle ICP-MS

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This contribution deals with the determination of gold and silver nanoparticles by substrate- assisted laser desorption inductively coupled plasma mass spectrometry (SALD ICP-MS) **[1].** Water suspensions of the both silver and gold nanoparticles of different sizes (20, 40, 60 and 80 nm) were deposited onto a polyethylene terephthalate glycol (PETG) plate using a commercial micropipette. After the evaporation of the solvent, the PETG plate was transferred into the commercial ablation chamber. Dried droplets containing nanoparticles were irradiated by Nd:YAG laser (213 nm). Ablated nanoparticles were carried from the ablation chamber by helium into the ICP plasma and analyzed by mass spectrometer in a single particle mode. In order to gain the highest transport efficiency for nanoparticles of each size, the conditions of analysis including laser fluence, laser beam scan rate and carrier gas flow rate were optimized. Measured transport efficiencies were in the order of tens percent. The advantages of the developed method are low sample volume consumption, possibility of the archiving of the sample and outstanding sensitivity in the order of units of silver or gold nanoparticles.

Keywords: SALD ICP-MS, nanoparticles, transport efficiency

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MP-54 Development of a low dispersion laser chamber for ultra-fast, automated imaging of biological and geological materials

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Recent developments in laser ablation have focused heavily on the development of sample chambers and interfaces with ICP-MS. The primary aim of such developments has been to reduce aerosol dispersion for faster particulate washout **[1-3]**, whilst retaining spatial reproducibility **[4]**; both important considerations for imaging and quantitative analysis.

Through these holistic approaches, it has become apparent that, although the universally applicable ablation chambers such as the TwoVol2 (*ESL*) are fit-for-purpose for most analysis; to achieve ultimate performance for a given need, then application -specific chambers are required. Here we present the development of a new ablation chamber for ultra-fast, high-throughput, automated imaging and analysis, of biological and geological materials. This low-volume chamber, coupled to the dual concentric injector (DCI) **[5]**, provides high-speed analysis whilst facilitating high-sample through-put using ESL's automation technology and an efficient purge. High resolution images are achieved using a combination of high accuracy nano-stages, short particle residence time (washout), the small spot sizes of the NWRimage and its high repetition rate. The chamber design ensures reproducible and consistent signal response across the entire sampling area due to the chamber-within-chamber concept (constant sample-to-outlet distance), optimised gas flow dynamics and an efficient purge.

Keywords: laser ablation, laser cell, laser chamber, imaging, bioimaging, geoimaging, fast washout

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MP-55 Coupling digital microfluidics with ICP-MS for single nanoparticle or cell analysis

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We propose to integrate an optimized digital microfluidic device with an inductively coupled plasma mass spectrometer (ICP-MS) in order to chemically and individually characterize inorganic nanoparticles or cells. Digital microfluidics consist in creating well-defined emulsions (droplets) on a chip. For ICP-MS coupling, aqueous droplets are formed in a continuous phase of volatile organic solvent that is eliminated by vaporization in the introduction system. A procession of monodisperse droplets in size, frequency and velocity is then introduced in the spectrometer and analyzed sequentially. We focus on chip design and chemical formulation. The device is based on a PDMS chip creating water or hydrochloric acid droplets inside a non-fluorinated organic solvent. The droplets are formed in a flow focusing junction: the aqueous interface is destabilized by the surrounding fluid (organic solvent) in a reproducible manner leading to a droplet formation. In some cases a second junction downstream can separate the distance between droplets. With this design and the chemical formulation chosen droplet diameter can be tuned between less than 10 µm up to 50 µm with frequency between 1 and 50Hz.

Keywords: digital microfluidic, single particle, single cell, hyphenated

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MP-56 Using online-LASIL for stoichiometry determination of Fe doped $SrTiO_3$ thin films

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$SrTiO_3$, a perovskite-type oxide, is a well investigated material used for resistive switching, as an electrode in fuel cell applications and generally as a model material for many studies in the field of solid state ionics. The electrochemical properties of Fe doped $SrTiO_3$ (Fe:STO) thin films deviate significantly from nominally identical bulk samples – an effect, which could not be explained in literature so far. Small compositional variations, which may be caused by tiny differences in the deposition conditions, are suspected to be the reason for these severe differences. Since the electrochemical properties are influenced and tailored by dopants, a determination of the stoichiometry is necessary.

The conventional approach consisting of a wet digestion and a subsequent liquid analysis for stoichiometry determinations has some drawbacks: it is time consuming, contaminations can be introduced at manual handling steps and bulk information is accessible only. In special cases, it is required that substrate and thin film are the same material. For these samples, the conventional wet digestion approach is not possible, because material from the substrate will be dissolved too and influences the result.

Here we present an application of the online laser ablation of solids in liquids (LASIL) technique for stoichiometry determination of Fe:STO. In this technique the He carrier gas of the conventional LA-ICP-OES method is replaced by a liquid (*e.g.* H_2O) to transport the particles produced at the ablation event into the detection system. With this advancement, it is possible to avoid a time consuming and error prone sample pretreatment. Furthermore, the use of liquid standard solutions for signal quantification is possible. In this contribution, Fe:STO thin films were produced by pulsed laser deposition (PLD) with different preparation parameters and subsequently analyzed for their electrochemical and analytical properties. For stoichiometry determination a conventional wet digestion of the thin films as well as the new developed online, LASIL technique was used and the results compared.

Keywords: online, LASIL, laser ablation of solids in liquids, complex metal oxides, CMO, STO, thin films

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MP-57 Isotopic, multi-elemental and nanoparticle micro-analysis with a new micro-flow uptake device for direct injection nebulization in ICP-MS

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The developed analytical setup successfully allowed ICP-MS micro-analysis at low micro- flow rates (10 $L.min^{-1}$) onto two different instruments.

First, a dual-loop displacement pump fed by an Ar low mass-flow meter (*ca.* 15 to 1000 $L.min^{-1}$) delivers a stable low velocity flow of carrier solution (typically HNO_3 2%) to a six port injection valve connected to an auto-sampler (SC-FAST, ESI) equipped with a micro-volume loop (20 L). Secondly, a high efficiency demountable direct injection nebulizer (d-DIHEN, Analab **[1,2]**) plugged in the torch, instead of the regular injector, nebulizes the sample in the plasma.

This fully automatized system was tested on: i) a MC-ICP-MS (Neptune, ThermoScientific) for boron isotope measurements at concentrations down to 5 ppb and ii) an HR-ICP-MS (Element II, ThermoScientific) for ultra-trace analysis around ppt level and gold nanoparticle characterization down to 5 nm with very high efficiency.

The presented analytical development will have innovative applications in the field of analytical chemistry, environmental sciences and geochemistry.

Keywords: ICP-MS, micro-volume, micro-flow, gas displacement pump, direct injection nebulization, boron isotopes, multi, elemental analyses, nanoparticles

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MP-58 Online microdroplet calibration for size and concentration determination of nanoparticle mixtures by ICP-TOF-MS

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Widespread use of engineered nanoparticles (NPs) continues to increase the risk of NP emission into environmental and biological systems. Better characterization and quantification of NPs in these complex matrices requires robust and high-throughput measurements. To this end, single particle SP-ICP-TOF-MS is a promising approach that enables multiplexed detection and quantification of diverse metal and metal-oxide NPs **[1]**. In SP-ICP-MS, accurate NP size and particle-number concentration (PNC) determinations are made possible by external calibration of element sensitivities and measurement of sample uptake rate into the plasma with standard NPs. Here, instead of these external calibration approaches, we present an online microdroplet calibration strategy to size and count NPs in a single step. In our system, we use a dual-sample introduction approach **[2]** in which individual microdroplets containing known element concentrations are merged into the aerosol generated by a pneumatic nebulizer (PN) and introduced into the ICP. Microdroplets are used to determine elemental detection efficiencies (counts.atom^{-1}) and calibrate for mass of NPs introduced via the PN. Additionally, by spiking a known concentration of cesium (Cs) into the NP-containing samples, and detecting the nebulized and microdroplet-contained Cs, we are able to calculate sample uptake rates into the plasma for every sample. As a proof-of-principle, we spiked commonly used metallic and metal-oxide NPs into several challenging matrix fluids and analyzed the NP suspensions by SP-ICP-TOF-MS with our online microdroplet calibration scheme. To evaluate the influence of plasma conditions on the simultaneous quantitation of mixtures of NPs, we also performed a multi-parameter investigation of ICP conditions. Results from these experiments demonstrate accurate sizing and PNC determination of NP mixtures even with non-optimum ICP conditions and the presence of severe matrix effects. As an example, we are able to correctly size NPs even when analyte signal is attenuated 80% with PBS matrix. We assess the performance of online microdroplet calibration for SP-ICP-TOF-MS and discuss implications of this system for NP quantification in complex environmental and biological samples.

Keywords: ICP -TOF-MS, SP-ICP-MS, nanoparticles, online calibration, transport efficiency, matrix effect

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MP-59 Applications of FFF combined with ICP-MS to nanoparticle and colloid measurements in the environment

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Field-Flow Fractionation (FFF) and ICP-MS together is a powerful combination of analytical techniques that can be used for characterization of nanomaterials. As a hyphenated system, FFF-ICP-MS generates an elemental-based size distribution over a broad size range. It can also provide elemental distributions which helps to study particles chemical composition as a function of particle size **[1-6]**. Collection of FFF fractions can be analysed by single particle ICP- MS (SP-ICP-MS) for additional information on particle size.

Determining the environmental concentration and physicochemical form of nanoparticles (NPs) released from nano-enabled products is an important component of the risk assessment of nanotechnology. One important form of NPs are heteroaggregates formed with background colloids present in the environment. Another is NP-polymer fragments that are released during the use and disposal of polymer nanocomposites. NPs that contain metals can be quantified and sized using SP- ICP-MS. When these NPs are associated with other materials (*i.e.* heteroaggregates and polymer- coatings), the size determined by SP-ICP-MS will not be the same as their hydrodynamic size. Analysis by SP-ICP-MS of fractions collected from FFF separations provides a means to determine the NP form more fully. This presentation will contain details of an examination of Ag-NPs heteroaggregated to silica colloids (model natural colloids) and Au particles coated with polymer, the latter being a model for polymer-NP fragments. Complimentary results were obtained for centrifugal FFF and asymmetrical FFF coupled to SP-ICP-MS.

Use of a 300-Dalton polyethersulfone FFF membrane to separate dissolved (*i.e.* < 0.45)

Keywords: field flow fractionation, nanoparticles, environmental, ICP-MS, single particle ICP-MS

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MP-60 Single-cell analysis enabled by ICP-TOF-MS

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Single-cell analysis is a growing research field. In contrast to the "CyTOF" instrument, where only elements with an m/z value between 75 and 209 can be measured, the *icpTOF* 2R from TOFWERK AG (Thun, Switzerland) enables the quasi-simultaneous measurement of all elements with an m/z value between 2 and 257 with mass resolving power of 3000 and 6000 (FWHM definition) providing information on biologically relevant elements from the lower mass range. In this work, we used this potentiality to combine the information gained from labelling cells with the information about trace elements at cellular level. Yeast cells labelled with *e.g.* cisplatin were measured for method validation. Analytical figures of merit (including transport efficiency) were addressed using different introduction systems.

Keywords: ICP-TOF-MS, single cell analysis, labelling, transport efficiency

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MP-61 Development of a new direct injection nebulizer for single-particle/cell ICP-MS

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Single-particle/cell ICP-MS has been widely used in various research and applications. In efficiently analyzing particulates (i.e. nanoparticles and cells) using the technique, a high transport efficiency (TE) of aerosol including particulates into plasma is ideal for reliable analysis, though it is difficult to accomplish with conventional sample introduction devices due to their low TE. To realize high TE, total-consumption sample introduction devices can be used, by which fine aerosol is transported into the plasma through a drain-less spray chamber, and thereby 100 % TE is theoretically obtained. However, 100 % TE is practically difficult to obtain, probably due to gravity settling of particulates (especially those having larger sizes than aerosol size) during their transportation through the spray chamber. Direct injection nebulizer is an alternative sample introduction device having a potential to realize 100% TE even for larger-sized particulates. However, as for commercial direct injection nebulizers, stable signal acquisition in ICP-MS is difficult to accomplish, mainly due to their coarse and wide aerosol size distributions.

To overcome this issue, we developed a new direct injection nebulizer having some structural advantages to ensure narrow aerosol size distribution and stable signal acquisition in ICP- MS. A home-made concentric nebulizer (2 mm in outer diameter) was inserted into a plasma torch injector (2.5 mm in inner diameter) with a gas port, and fixed at the center axis of the nebulizer using a spiral tube outside the nebulizer. The nebulizer nozzle has a unique structure enabling both fine aerosol generation and narrow angle nebulization. A sheath gas is introduced from the gas port of the injector and flowed into the plasma through the spiral tube, by which the central channel of the plasma is made more stable than the cases with the commercial direct injection nebulizers, and thereby the plasma is easily ignited and kept stable.

We evaluated the aerosol size distribution and ICP-MS signal stability when using the developed direct injection nebulizer. At the sample flow rate of 50 L.min^{-1} and nebulizer gas flow rate of 0.35 L.min^{-1}, the obtained Sauter mean diameter ($D3,2$) and volume median diameter ($D50$) were 3.5 µm and 4.1 µm, respectively. At the sample flow rate of 10 L.min^{-1}, nebulizer gas flow rate of 0.35 L.min^{-1} and sheath gas flow rate of 0.45 L.min^{-1}, the relative standard deviation of the obtained ICP-MS signals with integration time of 0.1 s was 1.7 % (^{59}Co and ^{115}In) as a typical example. These results indicate that the developed direct injection nebulizer has superior fine aerosol generation capability and enables stable signal acquisition in ICP-MS.

In this presentation, we will also briefly introduce the single-particle/cell ICP-MS analytical results using the developed direct injection nebulizer.

Keywords: direct injection nebulizer, cell, nanoparticle, ICP-MS, transport efficiency

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MP-62 Stable and radiogenic isotope ratio measurements of cave and marine coral samples using multicollector ICP-MS with a desolvating nebulizer sample introduction accessory

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Multicollector ICP-MS instruments are widely used in geochemistry for high precision isotope ratio measurements. Analyte element signal enhancement and/or mass spectral interference reduction (ex. oxides and hydrides) is often required for useful measurement of low abundant isotopes and mass-limited samples.

This work will describe the setup and optimization of an advanced desolvating nebulizer accessory for multicollector ICP-MS. Important benefits of this accessory include inert wetted nebulizer components for HF-containing samples, heated inert spray chamber and membrane desolvator for optimum sample transport efficiency, and computer control of heater temperatures and mass flow controllers (Ar sweep and nitrogen addition gases) for ease of tuning.

This nebulizer accessory combination with multicollector ICP-MS is especially applicable for geochronology such as U-Th dating, as is commonly used in dating cave (speleothem) and marine coral calcite and aragonite samples. Complete system parameters and dating measurements will be presented for representative sample types.

Keywords: nebulizer, geology, isotope ratios, multicollector ICP-MS

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MP-63 High volume in-line syringe dilution system for ICP-OES and ICP-MS

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A new automated in-line syringe dilution system has been developed to accommodate larger sample volumes needed for high flow applications or longer analysis times such as required of sequential ICP-OES instruments. The system utilizes flow-injection technology for rapid sample uptake and washout of undiluted samples, coupled with high precision syringe driven in-line dilution before injecting samples into the instrument. The continuous addition of an internal standard solution is provided in all cases. This results in the ability to perform inline, automated calibration from a single stock solution as well as automated dilution of samples which exceed the calibration range or fail internal standard control limits. Data and figures of merit demonstrating the accuracy and reproducibility of the system are presented here, as well as real-world application analysis of food and agricultural samples.

Keywords: samples, dilution, automation, calibration

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MP-64 Automated preconcentration and matrix removal for ultratrace determination of radium in environmental waters

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Radium is a naturally occurring element that originates from the decay chains of U and Th. Consequently, environmental waters, especially those that originate from areas with high U concentration, may contain trace amounts of Ra. Human activities such as the mining and processing of uranium or thorium may also result in elevated radium concentrations in discharge waters.

Due to its radioactivity and no beneficial biological role, even a low concentration of radium in environmental waters is hazardous to human health. As a result, the World Health Organization (WHO) and many national and regional authorities have developed regulations for the monitoring of radium in water, both for human consumption and for industrial processes or wastewater discharge. These regulations for radium in drinking water are extremely stringent, often below the detection capability of even modern ICP-MS instruments when used in direct analysis mode without any sample purification or matrix removal.

Alpha spectrometry or other analytical techniques may be used to determine Ra in natural waters, but they are slow (hours or days) and require extensive manual sample preparation. ICPMS is a preferred analytical technique due to its rapid analysis time and low detection limits. However, certain polyatomic interferences and matrix effects may cause erroneous results. Fortunately, various preconcentration and matrix removal techniques have been demonstrated in the literature to reduce or eliminate ICPMS matrix effects and remove matrix-based polyatomic interferences for the accurate determination of Ra in natural waters. However, many of these techniques require manual sample preparation and multiple, offline column extraction steps or unreliable inline column separations using peristaltic pump tubing.

The present work demonstrates an automated system for the ultratrace determination of Ra in environmental waters by ICPMS using syringe-driven preconcentration and matrix removal. Untreated or slightly acidified, high matrix environmental water samples may be directly analyzed by automatic standard additions or automatic external calibration. Detection limits better than 0.01 Bq/L (0.27 ppq) are achieved for 226Ra.

Keywords: radium, environmental discharge, automated extraction, ion exchange, column preconcentration, matrix removal, automation

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MP-65 Weighted averaging based spectrum processing scheme for skin cancer detection based on laser-Induced breakdown spectroscopy measurements

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In this study, an efficient spectral line weighted averaging scheme is proposed for detecting skin cancer from laser-induced breakdown spectroscopy (LIBS) captured spectrum. Instead of using raw intensity of the whole spectrum, several spectral lines of significant biomarkers for cancer detection can be pre-selected based on the reference of NIST database, such lines corresponding to the peaks of the biomarkers, and can be used for efficient and reliable classification. Due to the uncertainty in the raw spectrum, Lorentzian curve fitted area can be used for classification and shown to provide improved results. Alternatively, in this study, the weighted average measure is introduced to smooth the peak response, while maintaining the large separation of the response of cancer and dermis. The weights are obtained by discretizing the Gaussian curve with a fixed sigma and mean, which is later normalized to add up to one. In this way, the standardized mean distance measure between cancer and dermis captures, denoted as the mean distance square divided by the product of standard deviation of both classes, can be further increased, compared to the raw intensity. The proposed scheme is evaluated with LIBS captured spectrum from skin cancer and dermis cells, where the lines of K, Ca, Mg and Mn, are investigated for the distance measure. The results show the increase of distance by the weighted averaging for critical spectral lines, which show potential to improve detection accuracy. In addition, correlation coefficients are also investigated to provide the basis for selecting a set of most influential lines to be used for differentiating the response of skin cancer from the dermis. For performance evaluation of the proposed scheme, four different sets with cancer and dermis sample have been examined. The less correlated lines together with the weighted averaging can provide the basis for concise but powerful detection of skin cancer by selecting a set of spectral lines containing more information.

Keywords: laser induced breakdown spectroscopy, cancer detection, weighted averaging, normalized weights, correlation based analysis, most informative

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PLT-1 Orbitrap analyzer and plasma ion sources: could they work together?

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This talk presents first-hand a short but eventful history of Orbitrap mass spectrometry, from laying down the first principles to its current status as the leading mass spectrometric technique for high-resolution, high mass accuracy quantitative analysis. Based on trapping of energetic ions in electrostatic fields, this analyzer can provide high performance analytical characteristics only when it is highly integrated with the ion injection process. The advent of pulsed injection from an external ion storage device allowed the Orbitrap analyzer to enter mainstream mass spectrometry, initially as a part of a hybrid instrument.

Since its introduction the utility of the analyzer has been relentlessly extended by coupling with additional capabilities such as quantitative analysis, new fragmentation methods, different vacuum and ambient ion sources, imaging and ion mobility. Three major families of Orbitrap-based instruments take advantage of different combinations of these c@&apabilities, with numerous new modes of operation enabled by parallelization of detection and ion processing, and intricate coordination with different ion-optical devices, especially with a quadrupole mass filter.

Meanwhile, emphasis on interfacing to LC, GC and other separations over the last decades implied also that Orbitrap practitioners dedicated most of their attention to ion sources for analysis of complex mixtures of organic molecules rather than sources for elemental analysis. As the result, domain of plasma ion sources has been left underutilizing unique Orbitrap features.

The second part of the talk is devoted to exploring possible ways of correcting this misbalance and looking into possible synergies between Orbitrap mass spectrometry and plasma ion sources for several important applications. Among examples of such applications are multi-element trace analysis; ion sources with "cool" plasma; analysis of nanoparticles and aerosols; elemental imaging and others.

While tending to reply positively to the question in the title of the talk, the conclusion also discusses further improvements needed to make such combination really compelling for both academic and industrial analysts.

Keywords: orbitrap MS

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PLT-2 Highly multiplexed imaging of tissues with subcellular resolution by imaging mass cytometry

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Cancer is a tissue disease. Heterogeneous cancer cells and normal stromal and immune cells form a dynamic ecosystem that evolves to support tumor expansion and ultimately tumor spread. The complexity of this dynamic system is the main obstacle in our attempts to treat and heal the disease. The study of the tumor ecosystem and its cell-to-cell communications is thus essential to enable an understanding of tumor biology, to define new biomarkers to improve patient care, and, ultimately, to identify new therapeutic routs and targets. To study and understand the workings of the tumor ecosystem, highly multiplexed image information of tumor tissues is essential. Such multiplexed images will reveal which cell types are present in a tumor, their functional state, and which cell-cell interactions are present. To enable multiplexed tissue imaging, we developed imaging mass cytometry (IMC). IMC is a novel imaging modality that uses metal isotopes of defined mass as reporters and currently allows to visualize over 50 antibodies and DNA probes simultaneously on tissues with subcellular resolution. In the near future, we expect that over 100 markers can be visualized. We applied IMC for the analysis of breast cancer samples in a quantitative manner. To extract biological meaningful data and potential biomarkers from this dataset, we developed a novel computational pipeline called histoCAT geared for the interactive and automated analysis of large scale, highly multiplexed tissues image datasets. Our analysis reveals a surprising level of inter and intra-tumor heterogeneity and identify new diversity within known human breast cancer subtypes as well as a variety of stromal cell types that interact with them.

In summary, our results show that IMC provides targeted, high-dimensional analysis of cell type, cell state and cell-to-cell interactions within the TME at subcellular resolution. Spatial relationships of complex cell states of cellular assemblies can be inferred and potentially used as biomarkers. We envision that IMC will enable a system biology approach to understand and diagnose disease and to guide treatment.

Keywords: bioimaging

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KT-1 Coupling of the liquid sampling-atmospheric pressure glow discharge to orbitrap mass analyzers: changing the way we look at plasma source mass spectrometry

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Inductively coupled plasma mass spectrometry (ICP-MS) has long-been the stalwart technique for trace elemental analysis for over 35 years, for many good reasons. The ability to solve diverse problems on a platform that has "looked" the same since its inception brings along a great sense of reassurance, but perhaps also complacency and tunnel vision. Perhaps new ion sources and mass analyzers may allow to collectively look at whole new areas of science.

Over the last half-dozen years or so, this laboratory, with significant initial help from the Pacific Northwest National Laboratory, has put its efforts into the coupling of the liquid sampling atmospheric pressure glow discharge (LS-AP-GD) microplasma with Orbitrap mass analyzer systems. While initiated somewhat on a whim, the coupling was remarkably easy to execute with immediate payoffs in mass spectrometer performance realized over anything previously used in atomic mass spectrometry. Recently, the two institutions collaborated to affect a nearly commercial- quality ion source housing and microprocessor-based controller system. With this combination, the device can be implemented in a manner of minutes on existing orbitrap instruments.

In this presentation, we will present results of the LS-AP-GD/Orbitrap coupling from two laboratories; Clemson University and IPREM (Pau, France). From the Q Exactive Focus instrument in the Clemson laboratory, we will present extensive work on uranium isotope ratio determinations. Important control and data acquisition parameters will be pointed out, with product ratio data compared with those of commercial instruments. The mass resolving power of that instrument (75,000 – 100,000) permits the separation of species such as $^{236}U^{16}O^{2+}$ and $^{235}U^{16}O^{17}O^{+}$, which would cause erroneous results on any commercial ICP-MS. On the other end of the application spectrum, the microplasma is readily applied for whole protein analyses, including following HPLC separations. These two applications point to information never seen in ICP-MS.

More recently, collaborative works in Pau on an orbitrap Fusion Lumos, literally demonstrate capabilities never seen before. That instrument has a nominal resolution of 1 M ! We demonstrate the measurement of a 'holy grail' in geochronology, the mass separation of ^{87}Rb and ^{87}Sr. In fact, a mass resolving power of > 1.5M was realized. In addition, direct mass spectrometric evidence for the existence of Hg:Se-amino acid complexes, a topic of much recent speculation was obtained. In that case, a single spectrum shows the isotopic fine structure across the 1:1 bimetallic complex inclusive of the amino acids.

It is expected that this coupling is just now expanding the iris of applications of plasma source mass spectrometry, which will allow a *more detailed look* at more diverse, importantscience.

Keywords: LS-AP-GD, microplasma, orbitrap, isotope ratio, high resolution

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KT-2 The combination of labelled antibodies and ICP- MS for biomarker analysis: recent progress and remaining challenges for multiplexing

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The combination of immunoassays with ICP-MS is based on the modification of antibodies with artificial element labels. Similar to fluorescence colors, these antibodies can be labeled by metals such as lanthanides, iodine or even nanoparticles and act as an indicator for the target protein (antigen) in the biological sample. There are several advantages associated to the use of labeled antibodies in combination with ICP-MS. Some are: i) the possibility of making ICP-MS detectable molecules when the initial species do not contain heteroatoms that are ICP-MS measurable; ii) the amplification of the signal by incorporating multiple detectable elements per antigen; iii) not manipulating the molecule of interest with the labelling; iv) the possibility of multiplexing immunoassays based on the simplicity of "mass fingerprints". Some of these aspects have been addressed for the monoplexed detection of biomarkers in body fluids and cell cultures in our latest investigations and will be shown in the presentation. Among them, the iodination of antibodies or the use of DOTA-labelled species have been successfully applied in combination with ICP-MS for the determination of Fe-metabolism proteins. In addition, the possibility of further amplification of the detection has been studied by combination of PCR with ICP-MS in the so called immune-PCR coupled to ICP-MS. Some recent examples of this specific topic will be included.

Keywords: labelled antibodies, ICP-MS, amplificaction, multiplex, immune, PCR

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KT-3 Monte Carlo simulations to characterize low- count-rate signals in ICP-TOF-MS and applications to single particle analysis

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Single particle (SP)-ICP-TOF-MS is an approach for the multiplexed analysis of single metal and metal-oxide nanoparticles (NPs). Combined with an online-microdroplet calibration strategy **[1]**, SP-ICP-TOF-MS allows for simultaneous quantification of diverse inorganic NPs in complex / real-world matrices. In SP-ICP-TOF-MS, complete mass spectra are collected continuously at high speed (up to 1000 spectra.sec^{-1}) and elemental signals are extracted to identify and quantify analyte mass in single- and multi-element NPs. At this high time resolution, sufficient linear dynamic range is best achieved through the measurement of ion-detector current via fast analog-to-digital conversion (ADC) rather than ion-counting approaches. For instance, the ICP- TOF-MS instrument used here (icpTOF 2R, TOFWERK AG, Switzerland) combines microchannel- plate (MCP)-based ion-detection with 14-bit ADC. This configuration enables quantization of ion currents greater than 500 ions.isotope^{-1} in each mass spectrum (*i.e.* every 46 s). However, direct digitization of MCP signal also means that the inherent gain distribution of the electron- amplification process is measured and contributes to signal variation. This signal variation is especially pronounced for low-count signals and is of importance for the accurate counting and sizing of small nanoparticles that are difficult to separate from background ions.

In this study, we use Monte Carlo methods to model TOF-MS signal as a compound Poisson distribution, in which TOF-MS signals are the sum of Poisson-distributed numbers of ions that each independently sample the gain distribution of MCP detection. We find that this model adequately describes the measured variance of low-count TOFMS signals, which enables us to better understand and account for TOF-MS signal structure during data analysis. Because low-count TOF- MS signals are best described by a compound Poisson distribution-rather than classical Gaussian or Poisson distributions-new criteria for NP detection and quantification are required, and will be discussed. Accurate characterization of background can also be used to separate background and NP signals in a manner similar to the deconvolution approach developed by Cornelis and Hassellöv **[2]**. Through the measurement of analyte-doped microdroplets, we demonstrate that ICP-TOF-MS signal can be modeled well enough to quantitatively uncover particle-signal distributions buried beneath dissolved-signal backgrounds. We discuss how background modeling improves PNC determinations, and apply our approach for the for challenging analyses of NPs in the presence of high dissolved background.

Keywords: ICP-TOF-MS, single particle, microdroplet

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KT-4 Novel workflows for metal-based anticancer drug research enabled by ICP-TOF-MS

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Metal-based anticancer drug research is the ideal poster case to establish unique analytical workflows based on ICP-TOF-MS. The promise and the dream of single cell analysis identifying minor subpopulations that play a critical role in biological processes of a population of cells is at the threshold of heralding a new era of omics. ICP-TOF-MS is a key technology in this endeavor. We will address prime examples of single cell analysis, imaging analysis with high resolving power and high throughput multi-elemental analysis. We will discuss analytical figures of merit, challenges when developing quantification strategies and thereof resulting applications in preclinical and clinical studies. The presented samples cover tumor samples from cancer patients, biological fluids and advanced in vitro models such as 3D tumor spheroids. More specifically, we address single cell analysis of platinum, ruthenium and gallium (as contained in clinical established and candidate drugs) together with trace elements (e.g. iron, phosphorus, sulfur, copper).

Keywords: metallodrug, single cell, imaging

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KT-05 Detection and characterization of nanoparticles in soil-water plant environments

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In parallel to technological advances and ever-increasing use of nanoparticles (NPs) in industry, agriculture and consumer products, the potential ecotoxicity of nanoparticles and their possible accumulation in ecosystems is of increasing concern. Because scientific reports raise a concern regarding nanoparticle toxicity to plants, understanding of their bioaccumulation has become critical and demands more research. We focus here on the uptake and accumulation of different NPs in several plants. Isotopically labeled Ag-NPs, Cu-NPs and ZnO-NPs, synthesized and characterized in the laboratory, were used to enable increased sensitivity of NP tracing following exposure to representative plants. Results of uptake experiments in *Arabidopsis*, tomato and common reed grown in hydroponic cultivation, and also tomato plants cultivated in soil, will be presented. *Arabidopsis* showed uptake/retention of NPs that is more significant in roots than in shoots. Single particle ICP-MS and scanning electron micrographs and EDS of plant roots showed presence of Ag-NPs in particular, localized areas, whereas copper and zinc were found to be distributed over the root tissues, but not as nanoparticles. In addition, potato plants cultivated in soil under real environmental conditions were exposed to Au-NPs. Metal concentrations in all samples were measured with ICP-MS following acid digestion. Similar trends but different magnitudes of accumulation for each NP were found in the three different plants under hydroponic cultivation. Although roots were the main accumulation site of metal/NPs, low levels of Ag were recorded in tomato fruits cultivated in soil. Potato plants accumulated Au in roots, stems and leaves but not in tubers. The NPs were found to remain in the top (3 cm) soil layer and were not translocated to deeper soil layers. Analysis of NPs exposed to hydroponic medium and plants indicated that plants play a major role in solubilizing the NPs. SEM studies provided direct evidence of the presence of Ag-NPs and Au-NPs, respectively, in the roots of tomato and potato plants grown in soil.

Keywords: SP-ICP-MS, Ag-NPs, Au-NPs, Cu-NPs, ZnO-NPs

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OT-01 Analytical method development for nanoparticule characterization by SP-ICP-MS: beyond monometallic spherical particules

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The increasingly widespread application of nanomaterials brings about the need for the development of novel, versatile and powerful analytical methods for the characterization of NPs, which can then be used *e.g.* to monitor the presence of NPs in the environment or for the quality control of NP synthesis procedures. One of the upcoming NP characterization techniques is single (nano)particle ICP-MS, which utilizes the attogram-range detection limits of modern ICP-MS instrumentation and a statistical evaluation of the time-resolved signal profile. As is nowadays realized by more and more analysts, ICP-MS is not only capable of the individual detection of NPs, which leads to the size distribution, number concentration or compositional analysis of particles, but it can also provide a lot of additional information.

Our presentation will give an overview of some of our results obtained most recently (*e.g.* in the characterization of structured, morphologically or compositionally complex nanoparticles, which is intended to demonstrate the versatility, as well as the advantages and limitations of ICP- MS analysis of NPs. A performance evaluation of SP-ICP-MS, also including a comparison with more established characterization techniques (*e.g.* TEM, SEM-EDS, XPS, solution-based ICP-MS, etc.) and the demonstration of the potential in high time resolution analysis will also be provided. The materials systems studied in our applications include metallic and metal-oxide particles/nanocomposites, as well as biological nanoparticulate materials, catalysts, etc..

Keywords: nanomaterials, single, particle ICP-MS

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OT-02 Quantification of breast cancer biomarkers using immunohistochemically assisted imaging by LA-ICP- MS

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With over 1.6 million new cases of breast cancer reported in 2012, there is an enormous amount of pressure placed on diagnostic systems to ensure that optimal treatment regimens are provided **[1]**. Treatment can range from multiple sessions of radiation to hormone therapy and is dependent on the levels of biomarkers present in the tumour.

HER2, ER and PR are the major biomarkers associated with breast cancer and are regularly imaged and graded using immunohistochemistry (IHC). While this is a well-established technique, the immunohistochemical stains are currently interpreted by a subjective assignment of categories such as 0, 1^+, 2^+ and 3^+. Unsurprisingly, this introduces significant discordance with a recent study reporting an agreement of only 75% between 65 pathologists **[2]**.

An alternate approach for objective gradings of breast cancer biomarkers is immunohistochemically assisted imaging by LA-ICP-MS. Here, antibodies are labelled with a suitable metal tag during standard immunohistochemical procedures.

Tissue microarrays with known HER2 pathologist gradings were analysed by immunohistochemically assisted imaging with LA-ICP-MS. The metal tag was quantified with matrix matched standards and the resulting distributions were consistent with the gradings obtained by the pathologists.

Once IHC staining for each biomarker is optimised, the three biomarkers will be spatially quantified on the same section simultaneously to ultimately provide objective gradings for improved treatments.

Keywords: quantification, breast cancer biomarker, laser ablation, immunohistochemistry, metal tags, ICP-MS

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OT-03 Analysis of single cells transported via microdroplets using ICP-TOF-MS

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The capability of analyzing single cells has gained more and more importance during the last decades. Every cell population shows a cell-to-cell variability, which cannot be investigated by bulk measurements of samples containing a large number of cells. Besides the powerful technique called flow cytometry (FC), elemental mass spectrometry using inductively coupled plasma mass spectrometry (ICP-MS) provides the unique capabilities to quantitatively analyse certain elements in a biological cell or to assess the uptake of metals into single cells, which is especially in the field of metal-containing drug design and the implementation of nanoparticles for targeted drug delivery of major interest.

In ICP-MS, the cells are usually introduced into the plasma as aerosol generated with the help of a nebulizer. This leads to transport efficiencies, which are dependent on the size and size distribution of the droplets containing single cells **[1]**. Since each cell population shows a certain cell size distribution, *i.e.* the cell size can deviate for several microns from the average diameter, we expect the transport efficiency also to be dependent on the cell size and cell size distribution **[2]**. To which degree and how many cell fractions get lost during nebulization and transportation is still unknown and object of current research. So far, cells with small diameters have been studied **[3]**, which makes it rather difficult to study cell size and uptake effects individually. Furthermore, most applications have used sector field ICP-MS or quadrupole ICP-MS, which limits simultaneous multielement uptake studies into cells. Therefore, our cell studies were carried out using a microdroplet generator coupled to an ICP-time of flight-mass spectrometer (icpTOF, TOFWERK AG).

In this work, Chinese Hamster Ovary (CHO) cells with an average diameter of 13 µm were successfully transported via monodisperse droplets and analyzed using single cell ICP-MS to investigate the uptake of cytotoxic elements into cells. Every sampled cell was embedded into a droplet with the help of a so-called Autodrop Pipette (microdrop Technologies GmbH, Germany). It is equipped with an actuated piezo actuator, which is used to selectively emit droplets in the range from 50 to 90 µm. The cells were cultivated in an incubator shaker using a cell culture medium that has been spiked with cytotoxic elements such as Pb, Cd or Se **[4]**. Especially, Pb and Cd are systemic toxicants and show a high degree of toxicity causing serious damage to the organs at very low concentration levels already. The CHO cells were measured as suspensions in either phosphate- buffered saline (PBS) or water. The cell size distribution, which occurs naturally as a rather broad distribution (9 to 19 µm, Cedex HiResAnalyzer, Roche), was studied in detail. A workflow for the single cell analysis of CHO cells and various calibration strategies aiming to the quantitative determination of the cytotoxic element uptake in each individual cell will be presented.

Keywords: ICP-MS, ICP-TOF-MS, multielement, single cell, metal uptake, CHO, microdroplet, transport efficiency

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OT-04 Gadolinium retention in the human body following administration of gadolinium-based contrast agents: information obtained by elemental bioimaging

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Due to its paramagnetic properties resulting from seven unpaired f-electrons, Gd is frequently applied in magnetic resonance imaging examinations. Due to the acute toxicity of free Gd^{3+}, ligand ions based on polyaminocarboxylic acids are used to create thermodynamically stable linear or macrocyclic complexes. The highly water soluble Gd-based contrast agents (GBCAs) are known to be excreted fast and unmetabolized, mostly via the kidneys. Nevertheless, recent studies showed that Gd traces persists not only in animal but also in human tissues including the brain. Some major questions arise from such retention phenomenon: (i) what is the reason for retention of gadolinium from the very stable and water soluble Gd-based contrast agents?, (ii) what is the Gd-species retained ?, (iii) what is the influence of the structure of the GBCA on the retention of Gd ?, (iv) at what cellular structures is the Gd retained ? and last but not least, (v) what are the medical consequences of the Gd retention in some organs such as the brain?

Aim of this study was the development and application of analytical methods for the spatially resolved quantification of gadolinium traces in human brain thin sections of a patient treated with GBCAs. To reveal the distribution of Gd within the brain, the imaging technique laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied, allowing the localization and quantification of Gd. 10 µm cryosections of different brain regions were ablated line by line using a 213 nm Nd:YAG-Laser. For quantification, matrix-matched standards based on gelatine were prepared. The obtained information should help to answer at least some of the questions. In this presentation, we will discuss some preliminary results of our ongoing research.

Keywords: gadolinium retention, human brain, laser ablation, LA-ICP-MS, bioimaging

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OT-05 Analysis of titanium dioxide nanoparticles in food by triple quadrupole and high resolution ICP-MS in single particle mode

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Labelling for the content of engineered nanomaterials as ingredients in food is mandatory in the European Union since December 2014 in accordance with Regulation 169/2011. Enforcing proper labelling of "nano" poses several analytical challenges. This includes challenges in relation to sample preparation, the limitations of existing analytical techniques and the lack of validated studies and reference materials. In this context, we investigated food samples containing the food additive E171. E171 is titanium dioxide (TiO_2) and used as a white pigment. This effect is achieved when the particles are not in the nanosize. However, due to the broad size distribution of the powders, a certain fraction of nanoparticles can be present. Among the currently most widespread techniques for the detection and characterization of NPs in food is inductively coupled plasma mass spectrometry (ICP-MS) in single particle mode (SP-ICP-MS). The relatively easy implementation of SP-ICP-MS in state-of-the-art ICP-MS instruments (which can be otherwise used for metal analysis and speciation) makes it a promising technique for routine analysis despite some analytical limitations. We used a triple quadrupole and a high resolution ICP-MS to study chewing gum, chocolate candy and cake frosting. Further, we spiked reference TiO_2 particles to milk as an example of a calcium-rich matrix. The obtained sizes were compared with electron microscopy results. Repeatable determination of number-based particle size distributions was possible with both ICP-MS techniques. The median particle diameters were in the range of 130 to 200 nm. Besides comparing the results of the two ICP-MS techniques, the talk will highlight the general analytical challenges of single particle ICP-MS, including calibration and data analysis.

Keywords: food, nanoparticles, single particle, ICP-QQQ, HR-ICP-MS, titanium oxide

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OT-06 Dependence of LA-ICP-MS results on the preparation of biological and clinical samples

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Over last decades, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA- ICP-MS) has become a well recognized method allowing for investigations of elemental distribution over different types of solids including biological and clinical samples. A common preparation procedure which is relatively often proposed to be undertaken prior to laser ablation includes freeze drying performed in order to stabilize the investigated material. A possible influence of variable preparatory techniques on results of multielemental LA-ICP-MS analysis of biological and clinical samples was investigated in the project devoted to organic tissues exemplified by chicken liver tissue (ChiliT) and plaque samples (PlaQS). Samples of the same liver were prepared prior to LA-ICP-MS measurements in three ways: 1) n-ChiliT: no preparation 2) d-ChiliT: drying and 3) f-ChiliT: freeze drying (3 h and 17 h). The preparatory steps were performed in triplicates. Then, samples were subjected to LA-ICP-MS measurements (LSX-213, CETAC, USA coupled to Nexlon 300D, Perkin Elmer, USA). Argon was applied as a carrier gas. The results reflecting averaged transient signals registered during line ablation (n=7) from surface of n-ChiliT; d-ChiliT and f-ChiliT samples were compared. A significant decrease of S, Cu and Mn intensities could be observed for samples subjected to drying and freeze drying, wherein the milder conditions were, the more subtle changes were observed (drying vs. freeze drying). Prolongation of the freeze drying process (3 h vs. 17 h) was evaluated. It can exacerbate looses and, moreover, it is not always necessary because masses of samples did not vary after 3 h. Results obtained from model liver samples were referred to real samples of atherosclerotic plaque, where severe analytes looses were also observed (S, Cu, Pb).

Keywords: laser ablation, sample preparation, freeze drying, liver tissue

The presenting author is a laureate of EWCPS-2019 PhD student grant

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OT-07 Determination of total uranium amount in single particles by ID-MC-ICP-MS for characterization of particle reference materials

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The Environmental Sample Laboratory of the International Atomic Energy Agency (IAEA- ESL) routinely analyses the uranium isotopic composition of single uranium particles on cotton swipe samples collected during safeguards inspections to ensure the completeness of safeguards verifications in the respective facilities. Two methods are routinely used within the IAEA Network of Analytical Laboratories (NWAL) to perform this analysis - secondary ion mass spectrometry (SIMS) and thermal ionization mass spectrometry (TIMS), the latter in combination with fission track analysis for identifying and selecting particles of interest.

Certified reference materials in the form of particles that are characterised for their isotopic compositions and uranium amount are of great importance to guarantee confidence in this kind of analyses. For this purpose, a trilateral cooperation between IAEA-ESL, the European Commission - Joint Research Centre Unit G.2, Geel, Belgium (JRC-Geel) and Forschungszentrum Jülich, Germany (Jülich) was established to produce such reference material of uranium particles with monodisperse sizes in the low mrange.

In the framework of the production and certification of such particle reference materials, the IAEA-ESL performed verification measurements of uranium particle reference materials, which were produced at Forschungszentrum Jülich and are certified at the JRC-Geel in accordance to ISO 17034.

In this context, the uranium amount per particle was first measured by isotope dilution TIMS (ID-TIMS) at JRC-Geel and then verified by isotope dilution multi-collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) at IAEA-ESL. This presentation presents the analytical approach that was applied at the IAEA-ESL for the determination of the uranium amount per particle by ID-MC-ICP-MS.

Single uranium particles were selected and transferred by micro-manipulation at JRC-Geel and dissolved in nitric acid prior to shipping to IAEA, where the samples were spiked with a certified ^{233}U tracer. A Neptune "Plus" MC-ICP-MS (Thermo Fisher Scientific) with a high efficiency sample introduction system Aridus 2 (CETAC) was used to accurately measure the $^{233}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios in 3 $pg.g^{-1}$ solutions. The IRMM-072 standard series was used to determine correction factors for correcting the mass bias and detector yield. Two calculation approaches were applied at IAEA-ESL for estimating the corrections for natural uranium contamination, coming from sample preparation and/or reagent, in the single uranium particles measured by MC-ICP-MS.

These two approaches and the ID-MC-ICP-MS measurement results for uranium amount in single particles will be discussed and compared with the uranium amount measured by ID-TIMS at JRC-GEEL.

Keywords: single particle analysis, uranium, MC-ICP-MS, reference material, safeguards, IDMS

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OT-08 Hydrodynamic separation techniques coupled ICP-MS for characterization of gold nanoparticles and dissolved gold species in *in vitro* toxicological assays

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Gold nanoparticles (Au-NPs) are widely applied nowadays in biomedicine and other fields **[1]**. Nevertheless, there are still open questions about their impacts and toxicological studies are necessary. The first approach for these studies is the *in vitro* assays with cells grown in cell culture medium. During these studies, the Au-NPs can suffer different transformations that should be followed to get a correct interpretation of the toxicological results **[2]**. However, classical microscopic and spectroscopic techniques used for NPs analysis cannot provide this information and new analytical approaches are required. Among them, the use of separation techniques hyphenated to inductively coupled plasma mass spectrometry (ICP-MS) is a promising option recently proposed and still under development for complex samples. Thus, the aim of this study was the development of hybrid techniques based on hydrodynamic separation techniques, such as reversed-phase liquid chromatography (RP-LC) **[3]** and asymmetric flow field flow fractionation (AF4), coupled to ICP-MS for the study of Au-NPs and dissolved gold species (Au^{3+}) in cells incubated in cell culture medium (Dulbecco's Modified Eagle Medium, DMEM) used in toxicity tests.

The separation and acquisition conditions in the RP-LC-ICP-MS and AF4-ICP-MS were optimized and it was possible to detect transformations induced by DMEM on Au-NPs and Au^{3+}. Thus, the presence of the DMEM produces a shift towards larger hydrodynamic diameters, which suggests the formation of protein corona and/or aggregates/agglomerates. Oxidation of the Au-NPs was also observed. Moreover, the cellular uptake of Au-NPs was examined by complementary techniques and the nanotoxicity was assessed using viability assays. The identification of Au-NPs and Au^{3+} associated to supernatant and cells by the developed methods can contribute to a better understanding of the mechanisms of toxicity of the NPs.

Keywords: gold nanoparticles, AF4, liquid chromatography, toxicology, cell culture medium, cells

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OT-09 ICP-MS with microsecond time resolution: on recent improvements and the detection of nanoparticles in environmental waters

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In this presentation, analytical methods based on inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS) for ultra-trace detection of nanomaterials in environmental samples will be discussed. Selected results from a European research project termed FENOMENO will be presented with a special focus on recent developments for direct, fast and high-throughput nanomaterial characterization on a single particle level. FENOMENO is an integrative project aiming at an understanding of the impact of manufactured nanomaterials on the environment. Innovative analytical approaches are used to study the fate and effect of wastewater-borne NPs in aquatic ecosystems including analytical sensor systems, biochemical markers and ICP-MS.

The benefits of stand-alone single-particle (SP) ICP-MS for the detection and characterization of single nanoparticles (NPs) will be discussed. Instrumental modifications are not only helpful for total elemental analysis but also enable the detection, for example, of individual Ag, Au and TiO_2 nanoparticles with significantly improved size detection limits. The advantages and disadvantages of millisecond versus microsecond dwell times are critically discussed including potential measurement artifacts.

Because environmental concentrations of nanomaterials are at ultra trace levels, analytical methods often include sample preconcentration and acidification of samples before sample storage. One major challenge for research in the coming decade is clearly the preservation of chemical things as they are in the original sample. Also, nanoparticle toxicity towards aquatic organism is typically tested using standardized test media but the nanoparticle fate in these media over the course of the toxicity test is not routinely checked. Here, SP-ICP-MS will be an important tool in the future that can provide information on effective concentration and nanoparticle size in toxicity assays.

Keywords: single particle ICP-MS, microsecond time resolution

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OT-10 Quantitative imaging of dystrophin using immunohistochemical assisted imaging mass spectrometry

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Duchenne muscular dystrophy (DMD) is a terminal childhood illness characterised by the absence dystrophin, a protein that confers stability during muscle contraction. Dystrophin quantification is a critical outcome measure for therapeutic trials in DMD, where it is necessary to assess both the quantity and location of dystrophin expression to determine the functional outcome. Current analyses of dystrophin expression use western blot (WB) for quantification and immunofluorescence (IF) for localisation, however the lack of sensitivity and poor reproducibility of these techniques lead to questionable results in the use of dystrophin as a biomarker in DMD drug trials. The US FDA guidelines for Bioanalytical Method Validation state that the method must have a CV < 15%, which is not achievable with WB and IF at the low concentrations seen after drug trials or in samples with revertant fibres. An emerging alternative for protein quantification is immunohistochemical assisted imaging mass spectrometry, a technique based on the combination of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in combination with metal-conjugated antibodies. An anti-dystrophin antibody was labelled with ^{158}Gd before histological application to wild-type mouse quadriceps sections. The sections were then imaged concurrently with matrix-matched standards using standard LA-ICP-MS imaging protocols. The method was validated to comply with the US FDA requirements and further improved on the current combination of WB and IF with the quantification and localisation of dystrophin in a single experiment.

Keywords: bioimaging, biomarker, dystrophin

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OT-11 Laser ablation coupled to SP-ICP-MS can quantify size and number concentration of inorganic nanomaterials in soils

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Analysing engineered nanoparticles (NPs) in solid environmental matrices such as soils requires novel, sensitive and selective techniques. Laser ablation coupled to ICP-MS in single particle mode (SP-ICP-MS) may analyse sizes and numbers of NPs in soils. SP-ICP-MS has been optimized for aqueous solutions and allows to obtain size and number concentrations of suspended NPs, but this technique has not yet been optimized for non-soft tissues such as soils. A LA-SP- ICPMS method using a Nu Instruments AttoM sector field ICP-MS was developed to analyse the size and number concentration (in number per kg soil) of 20, 60 and 80 nm gold NPs that were deposited within different soil columns using column tests. Ablation laser energy and sample treatment and calibration methods of the combined set up were optimized, showing near 100 % recovery of particles during ablation and reproduction of expected sizes. Not only this is the first method to provide accurate number concentrations in solid matrices such as soils, the results indicate that it can also be used independent of whether the NPs were deposited as aggregates or as single particles. These insights can improve models predicting the fate of NPs for risk assessment of potentially toxic NPs or for improving efficacy of terrestrial nanotechnology such as nanofertilizers.

Keywords: environment, soil, gold

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OT-12 Investigation of uranium effects on neuron-like cells: an interdisciplinary analytical approach

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Uranium (U), the heaviest element naturally present in the Earth's crust at significant amounts, is ubiquitous, resulting in potential human exposure to small U amounts. Regardless the kind and the route of exposure, the brain is a sensitive target for uranium toxicity, as pointed out by several studies in the last few years **[1]**. Recently, neurological effects caused by U were suspected in humans. However, the U toxicity mechanisms inducing neurological alterations are little known **[1]**. In order to better understand U neurotoxicty mechanisms at the cellular and molecular level, an interdisciplinary analytical approach was undertaken to investigate the impact of small amounts of natural uranium (U_{nat}) on a human cellular model. To meet this aim, cutting-edge analytical methods were developed, such as quantitative chemical imaging by ion beam microprobe, high precision isotopic analysis by multicollection inductively coupled plasma mass spectrometry (ICP-MS), metalloproteomics by high resolution electrospray ionisation mass spectrometry (ESI-MS), following the recovery of uranium containing-proteins by different separation techniques.

SHSY5Y cells, used as human neuronal model, were differentiated into dopaminergic neurons and then exposed during seven days to U_{nat}. Cell viability assays were first performed, allowing to select non-toxic and slightly toxic uranium concentrations relevant for analytical studies, which are 1, 10, 125 and 250 mol.L^{-1} **[2]**.

The intracellular localization and quantification of U and its impact on essential trace elements homeostasis can provide clues for the identification of uranium incorporation routes and potential neurotoxicity mechanisms. For this, two complementary analytical techniques based on *in situ* quantitative analysis by ion beam and bulk multielemental analysis by plasma source mass spectrometry were implemented. Uranium quantitative subcellular distribution was determined by means of micro-PIXE (Particle Induced X-ray Emission) in neuron-like cells exposed to 10, 125 and 250 mol.L^{-1} of U. In any case, no uranium was observed into the nucleus of the neuronal cells, while uranium was distributed within the cytoplasm, but not homogeneously **[2]**. Multielemental analysis was carried out by ICP-MS, allowing the measurement of intracellular U amount, as well as endogen elements (P, Mg, Fe, Cu, Zn, Mn) in bulk cell samples. Concentration-dependent uranium uptake was demonstrated but in all the cases, less than 3% of U was incorporated by the cells. Moreover, the homeostasis of endogenous elements was not disturbed at low exposure U concentrations (1 and 10 mol.L^{-1}), while modulation of Cu, Fe, and Mn homeostasis was induced by intracellular U accumulation after exposure to higher concentrations (125 and 250 mol.L^{-1}) **[3]**.

The monitoring of isotopic fractionations in biological media has recently been shown as promising marker for disease diagnosis and element metabolism. In this field, high precision isotopic analysis in *in vitro* cellular models is an underexploited tool to help understand the processes leading to isotopic fractionations in living organisms or decipher cellular pathways of toxic metals. Then, the isotopic fractionation of U during its uptake by cells was studied, as well as the isotopic signatures of Cu and Zn in the extracellular and intracellular media. Given the small size of the samples, the low amounts of intracellular Cu and U amounts, and the complexity of the matrices, efforts were initially focused on the development and validation of a fit-for-purpose analytical procedure for high precision isotope ratio measurements of these elements **[4]**. The intracellular accumulation of U was accompanied by a preferential incorporation of ^{235}U by cells exposed to 1 and 10 mol.L^{-1} of U, whereas no significant isotopic fractionation was observed between the extra- and the intracellular media for higher exposure U concentrations **[3,5]**. In any case, the intracellular Cu and Zn isotopic signatures were not modified following U uptake **[3].**

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In order to identify intracellular proteins that selectively bind U and also the pathways impacted in response to U exposure, a non-targeted proteomic approach was applied. Lysates from control neuron-like cells and neuron-like cells exposed to 10 mol.L^{-1} of U were subjected to immobilized metal affinity chromatography (IMAC) and size exclusion chromatography (SEC) steps, respectively. Analysis of proteins in the collected fractions was performed by high resolution ESI-MS, allowing their identification and, in turn, to suggest chemical U species able to be formed within the neuron-like cells.

All together, results obtained by these interdisciplinary analytical developments are able to give information on the speciation of intracellular U, a key point to improve the understanding of the biochemical disturbances resulting from uranium toxicity in neurological system.

Keywords: uranium, neuron, like cells, imaging, isotopic analysis, metalloproteomics

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OT-13 Model studies of the uptake and behaviour of CeO_2 nanoparticles in radish (*Raphanus sativum L.*) using mass spectrometry techniques

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Due to their unique physical and chemical properties, the use of metal-based nanoparticles (NPs) in different areas such as medicine, cosmetics, energy or agriculture has exponentially increased causing their presence in the environment. As a result, NPs can interact with plants providing a potential pathway for human exposure and hence, their impact on edible plants and food safety needs to be investigated. Therefore, in the frame of food safety, the investigation of the behaviour of NPs on their interaction with edible plants is needed.

The objective of this study was the investigation of the uptake, bioaccumulation, and possible translocation of cerium oxide nanoparticles (CeO_2-NPs) in the model plant *Raphanus sativum* L. In the first step, the stability of CeO_2-NPs in plant growth media and after applying a standard enzymatic digestion procedure was tested. An enzymatic digestion method was next used in order to extract intact nanoparticles from the plant tissues without altering their properties. Once extracted, CeO_2-NPs were characterized by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). SP-ICP-MS technique allows the simultaneous determination of the particle size and particle concentration together with the dissolved metal concentration in the studied plant tissues. The total amount of cerium in control and plant samples was determined after mineralization by standalone ICP-MS. Finally, the localization of intact CeO_2-NPs in the plant tissues was studied by laser ablation ICP-MS (LA-ICP-MS).

The results shown that despite CeO_2-NPs can remain intact after cultivation and enzymatic digestion, a small degree of agglomeration was observed in the growth medium. However, the results obtained by SP-ICP-MS for the plant tissues after enzymatic digestion showed size distributions in good agreement with the standard of CeO_2-NPs used for cultivation, which led to the conclusion that plants do not take up the CeO_2-NPs agglomerates present in the medium. In the case of roots, a small degree of dissolution was observed what resulted in higher size detection limit of NPs. Good recovery values were obtained for both leaves together with stems (103.2%) and roots (102.7%).

Keywords: CeO_2 nanoparticles, single particle ICP-MS analysis, bioaccumulation, plants

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OT-14 The use of plasma-assisted techniques to unravel the genetics of metal storage in seeds

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The growth, development and in fine the productivity of plants is based on the fine-tuning of their mineral nutrition. The analysis of the mineral content of plants, for both macro- and micro- elements, requires the ability to analyze the atomic content of organs, a concept widely known as "ionomics". The modern approaches of genetics and genomics are currently in high demand of high-throughput analytical techniques able to meet this need, since the number of samples is dramatically increasing (several organs, growth conditions, stresses, many individual plants...). Moreover, the cross-regulation of many elements (Fe/Cu/Mn, K/Na/Mg...) also requires the use of multi-elemental approaches able to provide this dimension to the analyses.

Genome Wide Association Studies (GWAS) can allow the identification of genes that control a specific biological trait. The main constraint of this approach is the requirement of high throughput techniques able to analyze several hundred of samples needed to run the analyses. We will present two examples of the use of plasma-assisted analytical techniques to identify genes controlling the metal content in seeds. First, we developed a high-throughput method with microwave plasma optical emission spectrometry (MP-OES) to analyze the metal content (Fe, Cu, Zn, Mn) of seeds from the model legume species Medicago truncatula. This procedure, extremely efficient and easy to set up in a biological laboratory, has allowed us to identify key genes regulating Fe and Cu concentration in seeds. Second, we have used LA-ICP-MS to quantify metals (Fe, Cu, Zn, Mn) at the surface of seeds originating from 275 natural accessions from the model plant Arabidopsis thaliana. This approach was intended to identify genes regulating the partitioning of metals between the envelope and the embryo of Arabidopsis seeds.

In both cases, the use of versatile multi-elemental techniques in combination with genetic approaches has allowed us to identify new regulators of biological processes in a very efficient and cost-effective way.

Keywords: iron, seed, LA-ICP-MS, MP-OES

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OT-15 Technology-critical elements (TCEs): Source characterization and assessment of environmental exposure

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Technology-critical elements (TCEs) are increasingly released into the environment, but fundamental information is missing with regards to quantities, environmental cycles and potential health hazards. TCEs are considered as emerging contaminants that need to be controlled from initial mining to final deposition and recycling. The knowledge on TCEs fluxes, in-use dissipation and impacts on the environment and human health are poor and not uniform due to a constantly changing use in new technologies. The knowledge from national to global scales emerges only slowly, also because of remaining challenges in the analysis of TCEs due to their very low abundances in the environment. As a consequence, the data currently available are insufficient to allow profound statements on risk assessment.

Therefore, the composition of potential dissipation sources (*i.e.* electronic scrap) of TCEs into the environment, as well as sinks and degrees of exposure in the urban sphere (*i.e.* urban greening) were the focus of this study.

A comprehensive knowledge of the elemental composition of electronic products is essential for the assessment of potential metal demand, their impact during environmental cycling and deposition as well as future recycling possibilities. Due to the content of hazardous metals, electronic waste may also pose a risk to the environment and health if products are not treated accordingly at their end of life stage.

A versatile approach to determine the elemental content of more than 50 elements in different components of electronic devices on the example of smartphones was developed **[1].** The analytical protocol is based on accurate disassembly of smartphones, a single processing microwave-assisted acid digestion followed by ICP-OES and ICP-MS measurements. The contents of up to 57 elements could be quantified in the certified reference material ERM®-EZ505 electronic scrap. The validated method was applied to all metal-containing components of selected smartphones, excluding batteries. The method allows for the determination of metal contents in various parts of modern smartphones, providing the basis for the estimation and prediction of future metal usage and thus the comprehensive investigation of recycling and circular economy aspects.

In the second part of this work, the exposure status of TCEs in an urban environment by applying advanced analytical techniques based on inductively coupled plasma mass spectrometry (ICP-MS) is explored. The data will form the basis to systematically investigate the role of urban greening related to TCEs in the urban sphere of Vienna in the context of Green Public Health. Therefore, a preliminary study of leaves from two different green façades in Vienna with different degrees of exposure (residential street *vs.* highly used road) was accomplished. The total content and elemental distribution of a number of target elements was analyzed by ICP-MS. These first results prove that the concentration levels of the investigated elements are significant. Levels for most TCEs ranged from 5 to 500 $ng.g^{-1}$, with some elements (*e.g.* Ce, Sb, Ga, Ir) found at even higher levels. The feasibility to investigate within-plant spatial distribution was investigated using tandem–LIBS-LA-ICP-MS at the laboratories of Applied Spectra (Fremont, CA, USA). The elemental pattern within leaves grown at exposed vertical greening sites in Vienna show an accumulation of selected elements within the veins of the leaf and approve the potential to use chemical imaging techniques to study the accumulation of TCEs in selected plant compartments.These data will form the basis in order to interpret accumulation of TCEs in plant materials.

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Different elements are considered as technology-critical. In general, elements are considered as TCEs which are used in novel technologies (*e.g.* Ag, Ce, Ga, Ge, Li, Nd, Sb, Ti, Tl). Here, these were studied along with patterns of platinum group elements (PGEs: Ir, Os, Pd, Pt, Rh and Ru) and rare earth elements (REEs: Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Y, Yb).

Keywords: technology, critical elements (TCEs), electronic scrap, urban greening, Tandem–LIBS-LA-ICP-MS

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OT-16 Single cell analysis of selenized yeast using triple quadrupole ICP-MS

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Selenium is an essential micronutrient for humans and animals. It was thought to have cancer chemo preventive properties as early as the 1960s **[1]**. Selenium-enriched yeast is a common form of Se used to supplement the dietary intake of this important trace mineral. The optimization of the Se-incorporation during the yeast growth and the characterization of the final products in terms of the selenium chemical forms present is requested by regulatory agencies. For this aim, the development of suitable analytical methods that allow to obtain rapid information on the success of the biotechnological process is highly demanded.

In this work, a method based on single cell inductively coupled plasma mass spectrometry (SC-ICP-MS) was developed, using short integration times for highly diluted cell suspensions for the analysis of selenized yeast. Different microflow nebulizers combined with a total consumption spray chamber were tested for this approach. In general, they all permitted individual cell introduction with relatively high efficiency (around 20%) **[2]**. Additionally, the use of triple- quadrupole ICP-MS detection makes possible the monitoring of constitutive elements like phosphorus useful as cell markers. Analytical figures of merit are presented and the methodology is applied to the quantification of Se in individual yeast cells. Complementary techniques were used for the identification of the different Se forms present in the yeast samples.

Keywords: single cell, ICP-MS, triple quadrupole

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And now what? (Reprise)

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Born during WWII and now certifiably "older than dirt", Gary Hieftje was privileged to be involved in the field of analytical atomic spectrometry since the mid-1960s and to witness many of the most significant achievements in the field. Some of the critical developments include the rise of flame and furnace atomic absorption, the persistence of high-voltage spark emission spectrometry, the evolution of glow discharge spectrometry into a method for depth-resolved analysis, the introduction and widespread acceptance of both ICP atomic emission and mass spectrometry, the reintroduction of laser ablation and LIBS spectrometry and efforts to tame matrix interference effects in all these methods. The Hieftje research group was engaged in many of these areas and benefitted from a host of highly talented graduate and undergraduate students, postdoctoral associates, research associates, visitors, and collaborators. The role of several of these folks in fostering research advances in analytical atomic spectrometry will be highlighted in this presentation.

Keywords: Old fart, heritage, history, future

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TP-1 Assessment of hyperaccumulation of selected metals by native plants growing in polluted Peruvian post-mining areas

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Mining activities significantly contribute to Peruvian economy, since this country possesses the most important mines in the world. The position of Peru in the world ranking of mining production is very strong; it is the second producer of copper, silver and zinc worldwide and it occupies the first place in the production of gold, zinc and lead in the Latin America. On the other hand, there is a problem about the remediation of post-mining areas where high concentrations of metals in soil are a source of serious environmental pollution; some of the most affected areas in Peru include, among others, Cajamarca, Huaraz, Puno, Huancavelica.

The presented research involves assessment of native plant species growing in Peru in terms of their metal accumulation potential and the species involved in the process. The large scale sampling campaign resulted in collecting approximately 60 plant species and corresponding soil samples from 64 points in two study areas during the dry season. The concentration of metals have been determined by ICP-MS in individual plants organs and correlated with the data on metal content bound to different soil fractions (assessed by the Tessier method). In addition, the study of soils provided information on their status and the mobility of heavy metals.

The prospection for new metal hyperaccumulators - by the determination of a ratio between bioavailable metals content in soils and plant organs - will be also attempted in order to enlarge the spectrum plants potentially useful for environment-friendly phytoremediation methodology. Preliminary results on the identification of molecular species involved in metal accumulation will also be given.

Keywords: hyperaccumulation, plants, ICP-MS, environment, phytoremediation

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TP-2 Examination of heavy metal contamination found in raisins, sultanas and currants by ICP-MS

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Over the last few years, studies have found high levels of contamination in grapes and grape products such as juice and wine. Recent studies have been conducted showing the presence of arsenic in apple juices and wine. Arsenic based pesticides, particularly lead arsenate, were in widespread use around the world up until the late 1980's and 90s. Despite arsenic residue being recognized as a potential problem from the turn of the century, lead arsenate was one of the most widely used pesticides in the nation and was applied to millions of acres of crops through the 1940's. Lead arsenate was the most commonly applied pesticide in fruit orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, samples were obtained of popular organic and regular raisins, sultanas and currants from various stores in the US, UK and Germany. Samples were digested using microwave digestion and tested by ICP-MS to determine heavy metal contamination.

Keywords: food safety, contamination, heavy metals, ICP-MS

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TP-3 Contamination, adulteration and counterfeiting: an examination of sources and concentrations of heavy metals present in food, spices, beverages and drinking water

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On a daily basis, the average person around the world is subjected to doses of heavy metals from a variety of sources. One of the most insidious sources of routes of exposure is through the food supply. The World Health Organization contends that food may be the source of the largest contribution to the intake of heavy metals (especially lead). Many foods may naturally contain heavy metal compounds, from either natural biochemical processes or from bioaccumulation from the environment. Other foods and beverages become contaminated by natural, agricultural or industrial sources of heavy metals. Finally, there are food and beverage products which are intentionally adulterated or counterfeited with materials containing heavy metals. In this presentation, we will look at different sources of potential heavy metal exposure and their concentrations using studies conducted by ICP-OES, ICP-MS and LC-ICP-MS to determine the presence and content of heavy metals in a variety of food products including spices, herbal preparations, fish and beverages. In addition to the original research presented, we will compare other historical studies and public health findings to showcase the sources and concentrations of various heavy metals found in the food and water supply in order to build a more complete picture of heavy metal exposure through food and beverages.

Keywords: heavy metals, contamination, adulteration

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TP-4 Examination of elemental composition and toxic metals in bread spreads

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Many popular breakfast and bread spreads are natural products composed of fruit, nuts, seeds and yeasts. Children are frequent consumers of many of these popular spreads. Studies of individual spread components such as grapes, nuts and cocoa beans have reported significant amounts of heavy metal contamination. Lead arsenate was the most commonly applied pesticide in fruit and nut orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, various samples of bread spreads including fruit spreads, peanut butter, nut butters, yeast spreads and cocoa spreads were tested for heavy metal contamination. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination possible in these common foods.

Keywords: food safety, contamination, heavy metals, ICP-MS

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TP-5 Tracing source and mobility of metals and metalloids in a hydrosystem impacted by past mining activities (Morelos state, Mexico)

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The Sierra Huautla, located in the Morelos State, Mexico, is a biological reserve with historical mines of silver and lead. In this area, waters used by inhabitants as drinking water or for domestic uses were previously shown contaminated by arsenic (As). In this study, an integrated environmental survey was proposed both in waters (dissolved phase and suspended particles) and sediments (bulk and its different fractions) to better constrain the source and the mobility of As and other trace elements. Two areas of interest were selected: (i) the Nexpa River ecosystem to determine the local biogeochemical background, and (ii) the Huautla site to assess the impact of past mining activities on the quality of environmental samples (waters, sediments). In sediments from the Nexpa River, even if Ag and Cd concentrations were higher than the Sediment Quality Guidelines (SQGs), enrichment factors (EFs) higher than 5 and Geo-Accumulation indices (I_{geo}) higher than 3, the Pollution Load Indices (PLIs, accounting for 16 metals and metalloids) were close to 1 suggesting a global low contamination and no environmental risk in the vicinity of the Nexpa River. In waters from the Huautla area, TE contents were higher than the WHO limits for Al, As and Mn in bulk waters, but also in the dissolved phase of waters for As. As occurring mainly under dissolved species, speciation analyses were also performed and revealed the occurrence of an unique inorganic species, arsenate As(V), which is one of the most toxic forms. In suspended particulate matters (SPM < 0.45 µm) from springs, mines and drinking waters, Ag, As, Cd, and Zn revealed concentrations higher than SQGs, high EF (> 5) and high I_{geo} (> 3). EF > 5 and I_{geo} > 3 were also shown for Li, Mo, punctually Mn and Ba (drinking waters), Sr (springs), Pb (mines). Pollution Load Indices being close to 3, SPM from the Huautla district were demonstrated significantly contaminated not only by arsenic, but also by metals. Geochemical calculations (PHREEQC modelling) were performed to determine the origin of trace elements. Their occurrence were supposed to be related to oxidized sulfides (As, Cu, Pb), sulfates (Cu, Pb, Zn), carbonates (Pb, Cu, Mn, Zn and Ti) or sorption-desorption phenomena under hydroxides or oxihydroxides. All these results confirmed a great sanitary trouble in the Huautla area and a relevant environmental issue.

Keywords: trace element, arsenic, metals, contamination, water, sediment, mine

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TP-6 U-Pb dating of carbonates by fs-LA-ICP-MS

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The U-Pb dating is a well-established method applied to geological materials, for periods ranging from around 10ka to 500ka. Since carbonates are ubiquitous minerals in the crust and sediments, their accurate dating can bring very important constraints on the geological history of basins, faults, fluid flow or reservoirs. However, the low and variable contents in U and Pb of carbonates and their sensibility to U/Pb gain or loss after precipitation, make getting reliable ages a challenge. Actually, all ages published rely on nanosecond lasers linked to sector-field or multi- collector ICP-MS. Here, a femtosecond laser ablation coupled to an HR-ICP-MS (Element XR, Thermofisher) has been used for the direct measurement of U and Pb in calcite samples. The LRS (Linear Regression Slope) approach was used to calculate $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios with unprecedented precision (RSD < 0.5% before uncertainty propagation for NIST) and corrections factors were determined using NIST614 standard and a natural calcite standard respectively. Dating of calcite based on the use of imaging (to select areas of interest), and short transient signals will be presented.

Keywords: laser ablation, dating, calcite, geochemistry, HR-ICPMS

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TP-7 Determination of trace metals and organometals (Hg, Sn) in high altitude lake waters of the Pyrenees

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High altitude ecosystems are of primary importance for the preservation of the biodiversity. They are also essential to help sustain the economic development of touristic regions. These ecosystems are very unstable due to human activity and are already affected by climate change on both local and global scale. Various studies have demonstrated chemical contamination of anthropogenic origin in Pyrenean lakes and ecosystems. This contamination is due to both local pollution (mining, industry, road traffic) and atmospheric transport from regional or global pollution sources. Then, the use of alpine lakes as proxies of global environmental changes implies a deep understanding of their natural processes and physicochemical dynamics, always considering all perturbations due to seasonal variations, altitudinal gradient and the own properties of the lake. One of the possibilities in the study of alpine lakes is to focus on the presence and the fate of inorganic contaminants. Indeed, the dynamic of metals and metalloids is directly related to hydrology and geochemical processes, themselves sensitive to changes in environmental conditions such as temperature, atmospheric deposition or biological productivity. Even if several research projects have highlighted the presence and the impact of contaminants such as toxic metals, metalloids and organometals in Pyrenean ecosystems, the exact chemical cycle of these elements has been barely investigated. In this study, a seasonal sampling has been conducted in order to investigate the distribution and the fate of trace metals (As, Sb, Cd, Cr, Cu, Ni, Pb, Zn,...), mercury (monomethylmercury MMeHg, inorganic mercury iHg and dissolved gaseous mercury DGM) and tin (methylated and butylated tin) compounds within the water column of several alpine lakes, and how such contamination can be constrained by climatic, hydrological and local to long range anthropogenic inputs. Water samples were collected in June 2017, October 2017, June 2018 and October 2018 in 18 different lakes of the Western Pyrenees on both French and Spanish slopes to understand the spatial and seasonal variations of metals contamination within the lake ecosystems. During the first two sampling campaigns, spatial variability has been evaluated in each lake by collecting subsurface water samples at upstream, center and downstream. In 2018, the sampling of subsurface water at different time of the day in some of the lakes allowed us to investigate the diurnal variability of the contamination. Ultra trace analysis has been performed in these water samples and a special care has been taken during all the analysis process starting by a thorough cleaning of all the material in the laboratory, a careful and homogenous treatment of the samples on field and a proper storage prior the return to the laboratory. The analysis of trace elements was validated by blank determination and low limit of detection and was carried out by ICP-MS, whereas the mercury and tin speciation was determined by GC-ICP-MS.

Keywords: trace metals, Hg and Sn speciation, ultra-trace analysis, alpine lakes, water sample, ICP-MS, GC-ICP-MS

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TP-8 Development of complementary CE-MS methods for speciation analysis of metal based antifouling biocides in surface water

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All underwater surfaces are subjected to biofouling, which causes substantial encroachments e.g. for shipping. On the one hand, global shipping traffic can lead to spreading of invasive species, on the other hand biofouling causes a higher flow resistance of ships and thereby increasing fuel consumption and greenhouse gas emissions.

Until 2008, tin based antifouling compounds (tributyltin, TBT) were applied, but because of their persistence and severe toxicity on non-target organisms, these were banned nearly worldwide. Today, frequently used paints are based on Cu and Zn with addition of booster biocides for enhanced efficiency. These are organic pesticides, which can be analyzed rather easily, or certain metal based complexes like Cu and Zn pyrithione **[1]**. Some toxic effects of pyrithione complexes on non-target organisms, *e.g.* blue mussels (Zn pyrithione LD_{50} = 2.5 $g.L^{-1}$ **[2]**) and annelids (Cu pyrithione LD_{50} = 0.06 $mg.L^{-1}$ **[3]**), as well as possible bioaccumulation **[4]** were already reported.

Through transmetalation or biotic and abiotic degradation processes of the mentioned metal- complexes in the environment, cations from sediments can be made bioavailable again and species/transformation products showing altered environmental properties (*e.g.* enhanced bioaccumulation) can be formed. However, suitable analytical methods for investigating the environmental behavior of initial metal-based biocides and different species are missing.

This work presents a new method for zinc pyrithione speciation analysis based on capillary electrophoresis coupled to mass spectrometry (CE-MS), which allows investigations of the environmental behavior of metal-pyrithione complexes in surface water. Employing CE-ESI-TOF- MS, emerging species could be successfully identified. Because of purity issues regarding the standard substances, a complementary CE-ICP-MS method was needed to determine the actual concentration of calibration standards for CE-ESI-MS prior to quantification of zinc pyrithione species in samples. Release and degradation of zinc pyrithione from biocide containing antifouling paints in real matrices (surface water) were investigated successfully with these methods. Applying CE-ICP-MS, the transmetalation behavior of the PT ligand with several metals (Cu, Fe, Zn) could be studied.

Keywords: CE-MS, capillary electrophoresis, ESI-MS, ICP-MS, environmental speciation, zinc pyrithione, transmetalation

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TP-9 Trace- and ultra-trace analysis of high mineralized ground waters.

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This work is focused on developing emerging analytical tools for the investigation of high mineralized ground waters in the very diverse geological units of Austria's territory. The main purpose of the project is the extension of various projects currently processed by the Geological Survey of Austria and the Federal Ministry – Sustainability and Tourism of the Republic of Austria with the aim to methodologically re-asses and update geogenic background concentrations of national ground water bodies within the implementation of the EU Water Framework Directive 2000/60/EC and the EU Groundwater Directive 2006/18/EC, respectively, as well as national legislations. The analytical methods investigated involved ICP-SF-MS operated under clean-lab conditions in combination with on-line matrix-separation and analyte enrichment techniques. Thus, data representing metal background concentrations in Austrian ground waters at ultra-trace levels could be obtained for the first time. In addition, not only the metal concentration of the liquid phase was assessed, but also the contamination of the particulate phase (*i.e.* suspended solids) was addressed in a differential approach. A methodological approach for the determination of Hg, based on ID-CV-ICP-MS, will be presented. This approach has been shown to be a requirement for the accurate quantification of Hg in the low ng. L^{-1} range. Further, a novel method for the ultra-trace analysis of platinum group elements by ICP-MS after on-line matrix separation and pre- concentration based on solid phase extraction will be shown. Data obtained within a recently performed comprehensive survey will be presented.

Keywords: high mineralized ground waters, solid phase extraction, cold vapour technique, isotope dilution analysis

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TP-10 Trace metals in particulate matter emitted by marine engines – potential environmental and health impact

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Marine engines are the major source of atmospheric particulate matter (PM) with a global emission comparable to road traffic and aviation. Nearly 70% of shipping emissions occur within 400 km of coastlines and research suggests that marine engine PM may contribute significantly to local mortality and morbidity. Fuel oil typically used for operation of marine engines contains several transition and heavy metals that may be present in the smaller PM fractions, small enough to penetrate to and affect the human bronchi and alveoli. Therefore, we investigated the presence of metals (Ni, V, Pb, Cu, Fe and Al) in the emissions from marine engines following the combustion of
3 different types of fuel oils. Firstly, using angular darkfield scanning transmission electron microscopy (ADF-STEM) we observed deposition of metal particles on and/or in a close proximity of PM. Using hydrofluoric acid digestion and triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ) we quantified the total concentration of metals which significantly differed between the tested fuel oils. To assess bioavailability and thus potential health impact of metals emitted with PM, emissions collected on the quartz filters were subjected to sequential extraction and individual extracts were analysed using ICP-QQQ. The mobility of individual metals and hence their bioavailability will be discussed.

Keywords: black carbon, trace metals, ICP-MS, emissions, marine engine, environmental pollution

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TP-11 Speed up your productivity - High throughput measurement of drinking water

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For labs routinely measuring a large number of samples, sample throughput and the cost per sample are highly important. The unmatched sensitivity of the PQMS Elite allows to use shorter measurement times and still achieving a very competitive precision. Here, we report a high throughput method analyzing > 80 drinking water samples per hour according to the US EPA 200.8 which specifies the criteria for drinking water analysis by means of ICP-MS. In this study, 21 elements (+3 internal standards) were measured over 7 hours with an average RSD of 2.2 %. Interferences were removed using the patented iCRC technology and quality control samples were measured to verify accuracy, precision, robustness of the method. The recovery rates of the quality control samples were between 90-105 % during the entire measurement and were evaluated fully automatically by the AspectMS software. The user friendly software, the lowest argon consumption on the market and the unmatched sensitivity result in the highest sample throughput and lowest cost per sample making the PQMS the ideal solution for labs measuring routinely a large number of samples.

Keywords: speed, productivity, high throughput, drinking water

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TP-12 Reliability of the direct ICP-MS analysis of volcanic ash nanoparticles

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Nanoparticles (NPs) in environmental media are of different origin (soil erosion, volcanic eruptions, dust storms, wildfires, etc.). Natural NPs can be very hazardous for human health and local (even global) ecosystems due to their specific properties. NPs are usually digested to be totally dissolved in order to ensure the accuracy of the analysis. Since the acid digestion is accompanied by an important dilution, the determination of some trace element concentrations becomes limited because of the limit of quantification of the analytical instrument. Hence, the direct analysis of NP suspensions by inductively coupled plasma mass spectrometry (ICP-MS) may be an interesting alternative. Furthermore, the completeness of NPs decomposition in plasma during the direct ICP- MS analysis is not studied yet.

To confirm the reliability of the direct analysis of NP suspensions by ICP-MS, results should be supported by the data obtained from a second independent method; conventionally acid digestion followed by ICP-MS analysis is used. In the present study, the ICP-MS determination of major and trace element concentrations in nanoparticles of volcanic ash was carried out after either the direct analysis of suspensions of these nanoparticles, or the acid digestion of the suspensions. The results obtained were compared. Ash samples from different volcanoes were considered as test samples for this study. NP fraction of volcanic ash was separated by sedimentation from bulk samples.

For major elements (Al and Fe), the direct and indirect analyses lead to similar results for the three studied ashes. The same agreement is observed for the concentration of rare earth elements (Y, La, and Ce), which are also constituent elements of volcanic ashes. These results confirm the completeness of decomposition of nanoparticles of mineral matrix in plasma. Additionally, some trace elements (Cu, Sn, Tl and Pb), which are potentially toxic, were detected and their concentrations were determined using both sample preparation procedures. For all the major and trace elements, and/or matrices, the concentrations determined by both procedures are in agreement. The results obtained confirm the reliability of direct ICP-MS analysis of volcanic ash nanoparticles. The concentrations of elements measured by direct ICP-MS analysis are the same as determined in solution of NPs after their acid digestion under the most severe conditions.

Keywords: inductively coupled plasma mass spectrometry, volcanic ash, nanoparticles, environmental analysis, natural nanoparticles, direct analysis

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TP-13 Palladium determination after solid phase extraction on strongly basic anion resins

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Widespread usage of car catalytic converters causes increased emission of platinum group elements (PGEs) into the environment. In the new type of converters, among all PGEs, palladium is the most frequently applied. Growing emission of Pd urges monitoring of the changes of its content in environmental samples. It is especially important considering relatively high mobility and bioavailability of this element. The most frequently used method in the environmental studies is inductively coupled plasma mass spectrometry. However, during Pd determinations, intensive spectral interferences occur in the presence of such elements as Cd, Pb or Zn. As an alternative method, adsorptive stripping voltammetry can be applied, due to its low limits of quantification and a different mechanism of analyte determination. The range of applicability of both analytical methods significantly improves after implementation of an additional step in the procedure of sample preparation, which relies on Pd separation from the matrix by solid phase extraction. The most suitable eluent for both spectral and electrochemical detections showed to be ammonium buffer. The procedure of sample pretreatment, based on Pd retention on Dowex 1 resin and further elution with ammonium buffer, was applied before Pd determination in quartz sand sample received from one of the monitoring plots distributed along highways and exposed to traffic-related contamination.

Keywords: palladium, inductively coupled plasma mass spectrometry, adsorptive stripping voltammetry, solid phase extraction, Dowex 1, quartz sand

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TP-14 Development and validation of analytical procedures for reference measurements of mercury in marine environment compartments with direct and species-specific isotope dilution analysis and hyphenated ICP-MS techniques

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Mercury is one of the most hazardous element affecting the human health and entire ecosystem, because of widespread distribution and ability of living systems to accumulate it within the food chain. Due to high toxicity and depending of organic or inorganic form, mercury may cause the serious damages to organisms. In October 2013, representatives of the governments of 142-member states of the United Nations agreed on the Minamata Convention on Mercury, which entered into force on 16 of August 2017. A key factor in shaping the obligations under the Convention is to control the anthropogenic emissions and releases of mercury and its compounds across its lifecycle for protection reasons. There is no known safe exposure level for mercury in humans and effects can be seen even at very low levels. Therefore, the use of adequate and precise analytical procedures for its determination is essential. The application of hyphenated techniques based on the combination of high performance liquid chromatography (HPLC) for mercury speciation analysis or cold vapor (CV) generation for total mercury with inductively coupled plasma mass spectrometry (ICP-MS) for reference measurements is discussed in the present investigation.

The development and full validation of IDMS based reference procedures: direct ID-ICP- MS, CV-ID-ICP-MS and HPLC species-specific ID-ICP-MS for accurate determination of mercury species (total Hg and MMeHg) in different marine environment matrices (biota, sediment, seawater) and at various concentration level with the objective of achieving an uncertainty target on final results of 1.5 - 5% ($k = 2$) and traceable to the SI system of references values are presented in this study. Systematic assessment of all factors influencing the measurement results was done through this work. Modelling of the entire measurement procedures and the use of appropriate certified reference materials enable to assure the traceability of obtained values to the SI units: the mole and the kilogram. The obtained excellent agreement with the reference values from the International Atomic Energy Agency certification campaigns further validated the analytical protocols developed in this study for the determination of mercury in samples of marine origin.

Keywords: mercury, monomethylmercury, hyphenated techniques, reference measurements, ID-ICP-MS

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TP-15 Determination of methylmercury using liquid chromatography – photochemical vapour generation – atomic fluorescence spectroscopy (LC-PVG-AFS) – A comparison with ICP-MS.

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A reliable method for the analysis of mercury species is cold vapour generation of mercury coupled with atomic fluorescence spectrometry (AFS) or inductively coupled plasma mass spectrometry (ICP-MS). The most commonly used method of cold vapour generation involves oxidising all organic mercury species to inorganic mercury (Hg^{2+}), followed by a reduction to elemental mercury (Hg0) with tin(II) chloride or sodium borohydride. However, this method uses a plethora of chemicals which is costly and prone to error, as well as instrumental issues due to the complex wet chemistry necessary.

Another pathway is photochemical vapour generation (PVG), which has been used in the past in conjunction with AFS and ICP-MS as an alternative method of cold vapour generation. PVG has previously been applied to total mercury measurements using UV with formic acid and acetic acid. PVG promises a much simpler and more cost effective approach with fewer and more environmentally friendly chemicals, achieving results that are comparable to the chemical vapour generation approach.

Here, we apply acetic acid PVG of mercury to speciation measurements with LC-AFS to provide a simpler analysis of methylmercury in three selected matrices: seafood, hair and sediment. In total, 7 certified reference materials were analysed to assess the accuracy and precision of the method. A comparison was made between PVG and CVG methods, which showed that the PVG method provided sensitivities equal to that of the CVG method. In addition, 14 yellowfin Tuna samples were analysed using acetic acid PVG and compared with an analysis using GC-AFS, which showed good agreement of results between the two methods. In addition, the new LC-PVG-AFS method was compared to currently available ICP-MS methods to compare the sensitivity and reproducibility. Further analysis with and without vapour generation of mercury before ICP-MS detection has also been carried out.

Keywords: monomethylmercury, speciation, photochemical vapour generation, fish

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TP-16 Quantitative analysis of Pb in soils in multimedia environment using fsLA and ICP-MS

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Lead (Pb) is a cumulative toxicant that causes various diseases. If Pb accumulates in soils through industrial activities, it will cause soil pollution and consequently will affect body systems. Thus, it is important to determine Pb in soils, which is used as an indicator for soil pollution. ICP- MS is the powerful technique for trace elements analysis. Unfortunately, it is complicated and difficult to digest soils completely for ICP-MS. LA-ICP-MS which has advantages such as simple sample preparation steps and less time-consuming has become attractive over the past decades. This study aimed to quantitatively analyze Pb in mutimedia, especially in soil samples, by using ICP-MS and to test feasibility of fsLA-ICP-MS. Applying two analytical techniques to soil samples, the results estimated by fsLA-ICP-MS were compared with those of ICP-MS. It was confirmed that fsLA-ICP-MS is useful technique for determination of lead in soils with accuracy in the range of 91.6% to 115.1% and precision < 25.2%. Despite the inhomogeneity of soil samples, the results of ICP-MS and fsLA-ICP-MS displayed reasonable correlations with the determined concentration of Pb even if CRMs were diluted. Therefore, it is expected that fsLA-ICP-MS can be used for quantification of Pb in soils.

Keywords: lead, soil, laser ablation, fsLA-ICP-MS, ICP-MS

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TP-17 Application of ICP-MS/MS for determination of chromium in environmental matrices

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The presence of chromium in the environment is mainly connected with human activity as chromium is widely used in various branches of industry. Emission of dust and ash from industrial plants, discharge of wastewater into water and soil, and storage of solid waste produced during manufacturing processes, contribute significantly to the pollution of the environment by this metal. Chromium is present in the environment at two common oxidation states, as Cr(III) and Cr(VI). The physiological and toxicological effects of Cr(III) and Cr(VI) on biological systems are totally opposite. Cr(III) is an essential element for proper functioning of living organisms, while Cr(VI) shows mutagenic and carcinogenic effects. The maximal concentration of total chromium and Cr(VI) is regulated in various environmental compartments, *e.g.* in drinking water, surface water, wastewater and soil. In order to assess the quality of environment, the sensitive analytical techniques for determination of chromium are necessary. Among various spectrometric techniques, due to sensitivity, repeatability, wide linearity range of calibration graphs and low detection limit, ICP-MS is often used for this purpose. However, the determination of chromium by ICP-MS technique using the most abundant ^{52}Cr (83.8%) and ^{53}Cr (9.5%) isotopes suffers from spectral interferences caused by constituents of environmental samples (carbon, chloride or sulphur). The most common interferences are $^{40}Ar^{12}C^+$, $^{35}Cl^{16}O^1H^+$, $^{35}Cl^{17}O^+$, $^{34}S^{18}O^+$ and $^{36}S^{16}O^+$ for $^{52}Cr^+$ measurement and $^{40}Ar^{13}C^+$, $^{40}Ar^{12}C^1H^+$, $^{37}Cl^{16}O^+$, $^{35}Cl^{17}O^1H^+$, $^{35}Cl^{18}O^+$ and $^{36}S^{17}O^+$ for $^{53}Cr+$ measurement. For elimination of spectral interferences the application of cold plasma, mathematical correction equations or collision/reaction cells were proposed. In our work, in order to obtain accurate and reliable results of chromium determination in environmental samples, we propose the use of 8800 ICP Triple Quad MS spectrometer (ICP-QQQ, Agilent Technologies) equipped with an octopole reaction system (ORS3) in tandem MS/MS mode. Optimization of the chromium measurement conditions with the use of helium as a collision gas was carried out for elimination of polyatomic interferences. Ammonia and oxygen were also tested as reaction gases for the production of new molecules at m/z ratio different from Cr isotopes, which are free from interference. Under optimal measurement conditions, in the presence of helium, ammonia and oxygen as collision/ reaction gases, the sensitivity of the determinations and the limit of detections of chromium were compared. The developed methods were validated by analysis of certified reference materials and used for the determination of chromium in environmental samples.

Keywords: ICP-MS/MS, chromium, spectral interferences, collision/reaction cell, environmental samples

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TP-18 Determination of major and trace elements in geological samples by laser ablation solution sampling inductively coupled plasma mass spectrometry

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To overcome the major shortcomings in conventional inductively coupled plasma mass spectrometry (ICP-MS) analysis with sample introduction by nebulization, a new solution sampling method was developed using laser ablation (LA). With this sampling method, water-related interferences were greatly reduced, with oxides (ThO^+/Th^+) and hydroxides ($ThOH^+/Th^+$) production rates as low as 0.15% and 0.01%, respectively, which are similar to those obtained in membrane desolvation ICP-MS. Another important advantage of this method is that the matrix effects became insignificant in the ICP-MS analysis whether employing a matrix with the sample dilution factor varying between 80-2000 or an acid matrix ranging from 2% to 30% (v/v) HNO_3. Compared with LA-ICP-MS analysis of solids, this sampling method exhibited an approximately 100-fold improvement in analytical signal sensitivity and the detection limits for most elements were two orders of magnitude lower. Unlike solid sample analysis, the commonly observed time- resolved element fractionation during laser ablation was negligible in solution sampling by LA. With the widely used NIST 610 silicate glass as the external calibration standard, multi-element in a series of geological reference materials were successfully determined: the feasibility was verified with accuracies within 10% for 45 elements and most of the precisions reported as RSD better than 7%. Besides, due to the high tolerance of matrix effects, the consumption of acid and ultrapure water during sample preparation was reduced by 20-100 times compared to the conventional nebulization method. Solution sampling by LA provides an effective, simple, and comparatively environment-friendly method that combines both the advantages of solid and solution sampling methods.

Keywords: LA-ICP-MS, solution sample, water related interferences, matrix effects

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TP-19 Laser ablation inductively coupled plasma mass spectrometry for the quantitative analysis of pellets of plant materials

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The determination of the elemental composition of plants is of key importance to evaluate the nutritional status of crops or the level of toxic elements because plants are the first level of the food chain. Plant samples are generally acid digested for further analysis by ICP-OES or ICP-MS. This procedure is time-consuming and a direct solid sampling analysis would offer practical advantages such as rapidity, few contaminations and no reagent manipulation. For these reasons, an evaluation of laser ablation coupled with an ICPMS instrument for the direct analysis of plant material was carried out. Plant tissues from different origins were pressed into pellets and sampled directly with laser ablation equipped with a carousel of 20 positions. The aerosol was next analyzed by ICP-MS. The operational parameters of the laser ablation device (spot size, fluency, frequency…) were first studied. Next, calibrations for Cu, Cd, Fe, Mn and Zn were carried out using various samples with known composition and issued from proficiency schemes. Ca was used as internal standard. The limits of detection for the method ranged from 10 $g.kg^{-1}$ (for Cd) to the 2 $mg.kg^{-1}$ (for Fe). Different certified reference materials were used to check the accuracy of the calibration and measurements were performed with five replicates. The results were in good agreement with the reference concentrations and the precisions were generally below 20 %. The reported direct solid sampling method could provide a fast alternative to acid digestion for plant material analysis.

Keywords: plants, trace elements, laser blation, ICP-MS

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TP-20 Biomonitoring of titanium contamination in moss samples by ICP-OES

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Titanium dioxide nanoparticles (TiO_2 NPs) are widely used in the industrial products. The large applications of these nanomaterials would cause toxicity for living organisms and damage in ecosystems. For a better understanding of TiO_2 NPs contamination, we present the analysis of Ti in mosses from different European countries associated with the project BRAMM (biomonitoring of metal deposition by MOSS). Mosses are known to be good environmental indicators of contamination because these organisms effectively accumulate atmospheric pollutants. Approximately 500 samples of moss were analyzed for this study. Samples were put in solution according to two methods, using or not the hydrofluoric acid, to retrieve all the elements in a quantitative way. This reagent allows to know if the elements of interest remain adsorbed on silica often present in plants (between 0.1 and 10% of dry matter). Ti concentrations were measured using an inductively coupled plasma optical emission spectrometer with lateral view at 336.122 nm. The limit of detection was 20 $g.L^{-1}$. Concentrations of Ti in moss average 325 $mg.kg^{-1}$ and range from 38 to 3000 $mg.kg^{-1}$. These values are higher than those reported in mosses from Norway which average 53 $mg.kg^{-1}$ and range from 12 to 310 $mg.kg^{-1}$ **[1]**. It was no significant difference between the two digestion methods concerning the moss samples. HF appeared not necessary for mosses, probably poor in silica. However, significant difference in Ti concentrations was observed on the two reference materials (NIST 1547 peach leaves and NIST 1573a tomato leaves) used in each batch of samples. HF is then necessary for Ti determination in plant samples.

Keywords: moss, titanium, ICP-OES

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TP-21 Determination of heavy metals in certified fish samples using ICP-mass spectrometry

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Nowadays, fish and seafood consumption increases in order to feed billions of People. In fact, this foodstuff is a valuable and easy-to-access protein source. Moreover, its important content of omega-3 fatty acid, various vitamins and minerals make fish an increasingly popular food in various preparations (like sushi, tartar). Unfortunately, fish meat could also contain toxic heavy metal like arsenic, lead or mercury. Only a few part of these contaminants come from the environment (rocks, volcanic activity) most of them could be directly related to anthropogenic activities. This fish contamination by heavy metals is far from being an isolated challenge. In fact, a study conducted in 18 European Union (EU) Member States, Iceland, Australia and three commercial organizations showed that up to 8.2% of fish species had Cd levels exceeding the maximum limits in fish muscle according to FAO and EU regulations. In order to protect customers health, some regulations appeared in different area. Two groups of elements are distinguished: essentials but toxics in excessive amounts like Fe, Cu, Se or Zn and toxics like As, Hg, Cd or Pb. For the experimental work a Shimadzu ICPMS-2030 has been used and the analyzed samples used for this study is Fish Protein Certified Reference Material for trace metals (DORM-4) from National Research Council Canada.

Keywords: Heavy metals, essential elements, toxic elements, ICP-MS, food safety, food analysis, fish, food contaminants

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TP-22 Quantitative analysis of contaminants in beverages using ICP-mass spectrometry

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Strict and steady food control is needed to protect consumers against undesired contaminations and to guarantee a high level of quality. This can be achieved by enforcing maximum allowable concentrations of hazardous substances. For simultaneous quantitative determination of the inorganic elements in beer, wine and other beverages, ICP-MS is the preferred quality control tool. ICP-MS offers a high sensitivity (trace detection), a wide dynamic range and a high sample throughput. The Shimadzu ICPMS-2030 represents an easy and fast solution to meet this requirement. In this study a variety of commercially available beers, red and white wines and spirits are investigated. 14 different elements are simultaneously quantified: As, Cd, Cs, Cu, Cr, V, Fe, Mn, Ni, Pb, Se, Sn, Tl and Zn. Even though beer and wine is regarded as a difficult matrix, because of the high number of constituents, the recovery values for all the elements are between 95% and 105%. This recovery demonstrates that the ICPMS-2030 developed method has a high accuracy, regardless of element concentration.

Keywords: ICP-MS, food contaminants, heavy metals, food safety, beer analysis, wine analysis

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TP-23 Temporal variation of priority and emerging contaminants in sediment core from Kiel Bay, western Baltic sea

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In recent years, marine ecosystem has been subjected to increasing anthropogenic disturbance and a well-planned approach for knowing and understanding its ecological status is of key importance for sustainability. In this work, we present a complete study of trace elements (TEs) and Rare Earth Elements (REEs) variation in a well dated sediment core collected in Kiel Bay. This region is a shallow margin area of the western Baltic sea and like all coastal waters in industrialized countries, the region has been subject to increasing nutrient and metal loads.

We determined concentrations of 34 elements (major, trace and rare earth elements) together with other relevant parameters such as organic carbon and grain size in a 20 cm sediment core. In order to assess the possible influence of anthropogenic inputs, different indices were determined, such as enrichment factors, geoaccumulation index and pollution load index. In this respect, a key point was represented by the choice of background values used for the calculation of mentioned indices, showing that the use of general standards limits the possibility to highlight possible contamination, thus local background should always be preferable.

Thanks to the dating performed on the sample, it was possible to link the obtained results with the pollution history of the studied area. Results show that the highest enrichment of TEs occurred in the period between 1917-1970 especially for Hg, Cd and Pb. The study of Pb isotopic composition proved to be a valuable tool in the tracking of pollution source, revealing mainly Pb from coal burning in the layers in which the element showed the highest enrichment. Determination of MMeHg was also performed, showing as expected the highest content in surface samples with percentage of MMeHg ranging from 0.02 to 1.2% of total Hg. Results on REEs, which are nowadays considered as new emerging contaminants, did not show high enrichment attributable to anthropogenic influence, but provided useful information for future monitoring of the area.

Keywords: trace elements, lead isotope ratios, REEs, marine sediments. monitoring, Baltic sea

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TP-24 Distribution of Se in French forest ecosystems compartments

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The radionuclide ^{79}Se is of high radioecological importance taking into consideration its long half-life (2.8105 years) and its high potential to be incorporated into natural element biogeochemical cycle after potential contaminant exposure. The complexity of its behavior in environmental compartments is related to the coexistence of the element in different forms (organic and mineral) and states (solid, liquid or gas), in connection with biological and physicochemical conditions.

Numerous studies have emphasized the pivotal role of organic matter in retention and transformation processes of Se in soils. The stocks and the mobility of Se is strongly affected by the organic matter, which influences its conversion rates (inorganic *vs* organic) and controls its accumulation, recycling, so also its residence time in the environment. Depending on environmental conditions and the turnover of organic matter, soil can function as a source or a sink of Se.

The influence of eco-climatic conditions and the mechanisms of mobilization from the "soil's" organic reserves are currently poorly understood, as well as the time scales involved. Forests, as heterogeneous ecosystems rich in biodiversity, attracted a special attention in this project. The poster will present the study of Se distribution in forest soil compartments representative of different climate and vegetation conditions. The total concentrations in samples (litterfall, humus, soil) were measured by ICP-MS. Prior to the analysis, optimization of the Se soil extraction protocol using hot block digestion system was performed. The conditions of ICP-MS collision/reaction cell were adapted to reduce high interferences observed during Se analysis by ICP-MS in soil samples.

The content of Se in litterfall, humus and soil was determined in samples from 50 forest sites with six dominant tree species: oak (Quercus robur, Quercus petraea), douglas fir (Pseudotsuga menziesii), spruce (Picea alba), beech (Fagus sylvatica), pine (Pinus nigra laricio corsicana, Pinus pinaster, Pinus sylvestris) and fir (Abies alba). Samples from forest sites located throughout the French territory were provided by the Renecofor network. Results and data obtained allowed the calculation of the stocks of the element and the fluxes in soil and above-ground biomass in the sampling plots.

Keywords: selenium, forest, ICP-MS, cycle modelling

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TP-25 Method development aiming at the determination of mineral nutrients in vegetable tissues by MIP-OES to underpin agricultural research

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The present work aims at developing a straightforward and robust method in order to measure the content of mineral nutrients in vegetable tissues of lettuce, tobacco and acacia tree by microwave induced plasma optical emission spectrometry (MIP-OES), following acidic sample digestion. The analytes were divided into two groups, namely Al, B, Ba, Co, Cu, Cr, Fe, Mn, Mo, Na, Ni, Si and Zn, and the macronutrients Ca, K and Mg. This choice matched analytical efficacy, considering the calibration ranges in the equipment as well as their expected concentrations in the samples. The MIP-OES is a multielement spectrometric technique (4200 MP-AES, Agilent) that generates a magnetically excited nitrogen plasma, being the nitrogen supplied by air compressor. The instrumental parameters adjusted for determination of all elements were, pump speed: 15 rpm, sample uptake time: 15 s, stabilization time: 15 s, reading time: 3 s. A 22 factorial design with 3 central points was evaluated for each matrix, being sample masses of 0.5000, 0.3750 or 0.2500 g of the dried tissues and 8.0, 6.0 or 4.0 mL the tested volumes of a 3:1 nitric acid:perchloric acid mixture for digestion in the digester block. Its initial temperature of 50 °C was hold for the first 30 minutes of heating, then the temperature was set to 90 °C and after 30 minutes, the final temperature of 120 °C was kept for about 4 hours, when the release of white vapour ceased. The digested samples were left to cool at room temperature and the resulting digests were transferred to polypropylene flasks, adjusting the final volume with deionized water to 50 mL, which matched the 5% (v/v) acid content limitation for sample introduction when dealing with MIP-OES. The recovery range for all analytes for the addition and recovery tests, in two concentration levels, were mostly between 92.6 and 108.0% for acacia samples, 91.0 and 105.7% for lettuce and 88.9 and 106.3% for tobacco. Additionally, the surface response evaluation for the 22 factorial design presented non- significant effects for both tested ranges of mass and acid volumes for most analytes, although higher concentrations levels were obtained for the highest levels of samples mass and acid volume for some analytes, which were then chosen for future conditions for analysis.

Keywords: MIP-OES, vegetable tissues, essential elements, non, essential elements

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TP-26 Analysis of wines by ICP-MS using TotalQuant

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TotalQuant is a software feature unique to the NexION ICP-MS systems for quantifying 81elements in a sample by interpretation of the complete mass spectrum. Measuring the full mass range takes only a couple of minutes and the spectral interpretation itself takes a few seconds. During the TotalQuant analysis, each element is assigned a response value (cps.ppm^{-1}) which is updated when a calibration is performed. Even though TotalQuant is an ideal tool for semiquantitative analysis during method development, it can also be used for a final material characterization.

A large number of articles can be found in the literature discussing the chemical characterization of wines, teas and other drinks. These studies usually concentrate on two aspects: heavy metal contamination during the growth of grapes or leaves and contamination during the manufacturing process. In the last 150 years, toxic metal emissions have increased ten-fold, leading to air, water, soil, and food contamination. TotalQuant can be a rapid, convenient and valuable tool for the evaluation of the levels of contaminants and essential elements in food and environmental matrices.

TotalQuant can not only measure concentration of many elements, but it could use as a tool for fingerprinting and profiling wines based on the elemental composition. Such analysis could be used to assign the geographical origins of unknown wines and to highlight adulterated and fraudulent samples.

This poster will show TotalQuant results of wine analysis and their statistical evaluation using the SpotFire software.

Keywords: ICP-MS, semi quantitative analysis, foods, wines

α - Presenting author

TP-27 Accurate analysis of seawaters by HR-ICP-OES and ICP-MS

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The analysis of trace elements in seawater is one of the most challenging analytical tasks in the field of environmental monitoring – the trace element concentrations are usually quite low, often in the low ng.L^{-1} range, and the seawater matrix causes interferences from its high dissolved salt content (3.5% m/v).

For ICP-MS, the seawater matrix is challenging physically and chemically. Continuous nebulization leads to salt deposition on the sampler and skimmer cones, resulting in a loss in sensitivity and poor long-term stability. The chemical composition of the sea water matrix causes polyatomic ion interferences and non-spectroscopic interferences, particularly for the determination of the first-row transition elements.

For ICP-OES, the direct elemental analysis of saline matrices using ICP techniques in routine laboratories is challenging in respect to (i) achieving good signal stability with low signal to noise levels, (ii) ionization interferences of alkali and alkaline earth metals that often lead to intensity deviations in the range from 5 to 10% and (iii) maintenance issues, memory effects and short lifetime of glassware and clogging.

This work demonstrates that the combination of HR-ICP-OES and ICP-MS can provide a simple but accurate way to measure challenging matrices such as seawaters.

Keywords: ICP-OES, ICP-MS, seawater

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TP-28 Corrosion protection of offshore wind farms: a new potential source of inorganic contaminants for the marine environment?

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Offshore wind energy is a steadily growing sector contributing to the worldwide energy production. Offshore wind farms in the German North Sea and Baltic Sea are an integral part of the renewable energy transition in Germany and this energy sector is constantly growing. The impact of offshore constructions on the marine environment, however, remains unclear in many aspects. In fact, little is known about potential emissions from corrosion protection systems used for offshore structures.

A widely used and established method of corrosion protection, besides organic coatings, is "galvanic anodes" composed of Al and Zn alloys. By definition, the constituents of these anodes are "sacrificed" instead of the structural steel. Hence, the application of galvanic anodes results in the continuous emission of inorganic matter (*e.g.* > 250 kg Al-anode material per pile foundation and year and significantly more for other foundation types and converter platforms) into the marine environment. In order to evaluate systematically the emission load from corrosion protection used by offshore wind farms, (i) suitable tracers have to be identified and (ii) reliable analytical methods for their detection and quantification in marine compartments have to be developed and applied.

In this study, Al and Zn anode materials from several manufactures were characterized for the elemental and Pb isotopic composition using LA-ICP-MS/MS and LA-MC-ICP-MS. Therefore, methods based on solution-based as well as laser ablation analysis were developed and fully validated including calculations of combined uncertainties. The elemental compositions show high mass fractions of rare and/or environmentally critical elements such as Ga (130 $mg.kg^{-1}$), Cd (700 $mg.kg^{-1}$), In (230 $mg.kg^{-1}$) and Pb (20 $mg.kg^{-1}$). Furthermore, Al and Zn anodes can be clearly differentiated by their Pb isotopic composition. The $n(^{208}Pb)/n(^{206}Pb)$ isotope-amount ratios in Al anodes range from 2.0619 to 2.0723, whereas Zn anodes show $n(^{208}Pb)/n(^{206}Pb)$ isotope-amount ratios ranging from 2.0927 to 2.1263. Additionally, each individual anode material provides a manufacturer specific Pb isotopic composition, which allows clear differentiation between materials.

However, the determination of the identified tracers in the marine environment, especially in the seawater matrix, is challenging as the released components (*e.g.* Ga, Cd, In and Pb) occur in concentrations in the $ng.L^{-1}$ range. Consequently, in the second part of this study, a method for the analysis of selected trace elements in seawater was extended to the tracer elements In and Ga. The method is based on the coupling of the ESI sea*FAST* system to an Agilent ICP-MS/MS, yielding detection limits of 300 $pg.L^{-1}$ (Ga, Cd), 10 $pg.L^{-1}$ (In) and 100 $pg.L^{-1}$ (Pb). Finally, the validated method was successfully applied to a set of seawater samples originating from different wind farms located in the German North Sea. First results show gradients of elements such as Pb along the residual currents.

Keywords: offshore wind farms, corrosion protection, seawater analysis, ICP-MS/MS, MC- ICP-MS, laser ablation

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TP-29 Optimization of a HPLC mixed-mode column methodology coupled to ICP-MS for selenium speciation in natural waters

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Selenium (Se) is present in natural waters at ultratrace levels in multiple oxidation states (- II, 0, IV and VI). A better knowledge of Se behavior may be critical to understand some of the biogeochemical processes occurring in waters. This work describes the optimization of a methodology based on high performance liquid chromatography (HPLC) and inductively coupled plasma mass spectrometry (ICP-MS) for simultaneous analysis of oxidized inorganic Se species and reduced Se compounds in natural waters. An Agilent 7900 ICP-MS equipped with an octopole collision/reaction cell technology (to reduce polyatomic interferences) is used as detector. An Omnipac PAX-500 mixed-mode (anionic exchange and reversed phase) chromatographic column is employed for Se separation. Mobile phase, organic solvent, pH and other parameters like injection volume have been optimized for these analyses. Finally, an isocratic elution of 20mmol.L^{-1} ammonium nitrate adding 1% of isopropanol as organic solvent and 1mmol.L^{-1} of p-hydroxybenzoic acid as pairing agent was selected. As the composition of reduced Se compounds stills not well characterized, pH was adjusted to 8.5 with ammonia to maintain a similar pH to the one found in natural waters and avoid the alteration of the Se species during the analysis. Separation of inorganic Se compounds (selenite and selenate) was achieved as well as different Se amino acids such as selenomethionine and selenocystine among other species like the trimethylselenonium ion in less than 15 minutes. Detection limits were in the low ng.L^{-1} range for an injection volume of 300L. Robustness was tested in three different natural waters: a model lake with high content of organic matter, the pristine waters from the Pyrenees lakes and the high salinity waters of the Adour estuary. The analytical performance, advantages and drawbacks of this methodology will be discussed.

Keywords: selenium, speciation, HPLC-ICP-MS, environmental chemistry, natural waters

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TP-30 Seasonal variations on dissolved selenium speciation in Lake Kinneret

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Lake Kinneret is a monomictic and relatively freshwater lake in northern Israel. During the past decades, it has suffered changes in watershed channeling during the 90's and a decrease in nutrient loads and water inflow, these facts are related to changes in phytoplankton populations. This project studies the seasonal variations of total selenium (TSe) and selenium speciation from 2015 to 2017. During this period, one sampling per season was carried out; samples were taken in the watershed and at different depths of the lake to study the whole water column evolution. A comparison between this monitoring and the one carried out **[1]** may be useful to better understand how these changes are affecting the selenium (Se) cycling in the lake.

Concentrations of TSe, Se(IV), Se(VI) and reduced Se (Se(0) and Se(-II) forms) follow the structural features of the water column. The lake is holomictic during winter-spring period thus, depth profiles are homogeneous. Stratification begins in late spring and last for summer-fall period. During stratification, surface waters exhibit oxic conditions and higher temperatures in opposition to bottom waters that show oxygen depletion and remain around 16 °C. TSe average fluctuates between 100-160 $ng.L^{-1}$ for the period of study. Highest values of TSe are found in winter in opposition to lowest values found in summer. This correlates with Jordan River fluctuations, the main water inflow of Kinneret Lake. TSe range is similar to that reported **[1]** probably as a result of internal Se recycling processes. Se(IV), Se(VI) and reduced Se distribution along the water column prove the dominance of reduced Se in bottom waters, especially during the stratification period. In previous studies, much less reduced Se was reported. This difference may be associated to phytoplankton population changes or a change on phytoplankton productivity.

Keywords: selenium, speciation, HPLC-ICP-MS, environmental chemistry, monitoring, seasonal variations

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TP-31 ICP-OES assessment of silver distribution in plant material after exposure to capped Ag-NPs

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Engineered nanoparticles gained the greatest interest in wide areas of materials production and use. Among variety of produced nanomaterials, the most widely commercially used are silver nanoparticles (Ag-NPs) that are specifically applied in agriculture as antibacterial, antifungal and antioxidants. Despite the benefits that come with their applicability, the increasing concern about their impact on the environment is reflected through numerous research studies. For instance, the interactions between Ag-NPs and plants, the differentiation between ionic and particle specific silver, the morphological and proteomic changes are topics of greatest interest **[1,2]**. Plasma based spectrometry methods are the most exploited element selective techniques for the total silver levels determination in studies of Ag-NPs **[3]**. Inductively coupled plasma optical emission spectrometry (ICP-OES) provides sensitive simultaneous measurement of analyte emission lines in solutions of complex matrix and it was applied in our study of Ag-NPs exposure.

We used ICP-OES for quantitative determination of silver content in tobacco seedlings (*Nicotiana tabacum* L.), which were exposed to Ag-NPs stress. The capping agents such as citrate, branched polyethylenimine (bPEI), and polyethylene glycol (PEG) were used for stabilization of Ag-NPs in solution that consists of growth medium (Murashige and Skoog medium). The tobacco seeds were treated with capped Ag-NPs and ionic silver as $AgNO_3$ solution. After ten days of germination, the silver content was measured in the growth medium, in the seedlings tissue and in the residual precipitate. Digestion of crude samples was performed by microwave assisted acid digestion (HNO_3/H_2O_2). The accuracy of analytical procedure was tested by reference material CRM NIST-1573a. The most sensitive silver emission line of 328.068 nm was used for measurements. Detection limit (1.5 $ng.g^{-1}$) was determined using method blank that consisted of growth medium matrix. Concentrations of Ag in plant seedlings, growth medium and residual precipitate were successfully determined in the concentration range of Ag 2.5 - 27 $g.g^{-1}$. Rising of silver level in tissue was established in all experiments with Ag-NPs. The treatment with ionic silver showed drop of measured concentration after certain level. The variations between citrate Ag-NP, bPEI-Ag-NP and PEG-Ag-NP were noticed as different silver level in tissue after treatment with differently capped NPs. The comparison of measured results showed that the distribution of silver in plant tissue relates to initially applied silver species.

Keywords: Ag-NPs, capped nanoparticles, ICP-OES, tobacco seedlings

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TP-32 Determination of trace, minor and major elements in steel using the PlasmaQuantMS®

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Monitoring and controlling the level of trace element impurities in metals and alloys is important, as impurities can affect the properties of the metal and may degrade the functionality of the finished component. Other techniques such ICP-OES are used in a routine base to measure trace and major elements in metal samples. However, the development of high purity metals, such steels and Cr-V alloys, requires stricter control of a wide range of elements.

ICP-MS is an ideal technique for this analysis since the wide linear dynamic range allows for the determination of trace, minor and major elements simultaneously without the need for additional dilution or pre-concentration techniques resulting in a considerable time-saving.

In this work, two reference steel materials (CRM 466/1 – Austenitic Stainless Steel and NBS 363 Cr-V Steel (modified)) were measured by PlasmaQuant MS® after an efficiency digestion in topwave microwave digestion system by AnalytikJena AG. Masses of 0,1g of the samples (reference materials) were weighted into digestion vessels and 5 mL of aquaregia was added. The 60 mL vessels were closed and fitted into the rotor and digested at 210 °C for 20 minutes. After digestion completed and vessels cooled, the contents were transferred to 100 mL volumetric flasks and diluted to volume with deionized water.

All solutions were clear after digestion although a small quantity of white material, assumed to be silica, was observed in several of the solutions. This was filtered off before analysis.

A range of 29 elements from major (percent), minor (ppm) and trace (ppb) levels were determined in two CRMs. The results obtained clearly showed excellent agreement with expected values. In order to further validated the method, a spike recovery test at 50 ppb was carried out for the 16 non-certified elements. Excellent spike recoveries were achieved, with most elements within 90 to 110% recovery.

Keywords: alloys, steel, ICP-MS, microwave digestion

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TP-33 PlasmaQuantMS®: a precise, accurate and versatile tool

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A precise, accurate and a useful method was developed for 18 elements (Na, P, S, Mg, Al, K, Ca, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Mo, Cd and Pb) determination in three different types of matrices: two certified reference materials: tobacco leaves (INCT-PVTL-6), sewage sludge (CRM055) and a quality control material: vegetable puree (FAPAS QC T07207). All the three samples were previously digested in a microwave system (TopWave®) and measured in the same run without the need of recalibration or a specific method for each matrix. Each sample dilution was measured in three condition sets (Helium, no Gas and Hydrogen modes). Within one measurement, all condition sets were executed with switching times of 30 seconds. For data recording, five average values were calculated from twenty-five scans each, which were used for the calculation of one average value including standard deviation. Results within the range ppb to % showed great precision and accuracy with the methodology applied during the measurements. All the certified elements were within the certified control ranges (Z-score < 2), RSDs values were, in general, lower than 5% and recoveries were between 90-110% considering the three conditions used in the method. PlasmaQuant® MS delivered precise and accurate results, but also it behaves as a robust instrument able to run different matrices in the same sequence using the same calibration curve without the need of preparing different methods for different matrices. PlasmaQuant® MS with its superior sensitivity is able to detect small concentrations and is a highly suitable instrument for the determination of trace and major elements in all types of samples.

Keywords: ICP-MS, method development, sewage sludge, tobacco leaves, vegetable puree, CRM

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TP-34 Stability of silver-based nanoparticles at environmentally relevant concentrations in seawater monitored by SP-ICP-MS

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Due to the increasing use of silver nanoparticles in commercially available products and applications, silver nanoparticles are more and more released into the environment. This has risen the discussion about concerns regarding environmental compatibility of silver nanoparticles. Once released into the environment silver nanoparticles undergo various transformations and are finally transported into the sea. To be able to determine silver nanoparticles in environmental concentrations in such matrices the combination of cloud point extraction (CPE) and single particle ICP-MS as well as TEM-EDX for particle composition determination is a promising technique. As previous studies have dealt with much higher silver nanoparticle concentrations (> 200 ng.L^{-1}) **[1- 3]** than environmentally relevant or non-relevant coatings, such as poly(ethyleneimine) or poly(vinylpyrrilidone) **[2]**, we conducted incubation experiments in seawater using citrate-coated silver (CA@Ag-NP), silver sulfide (Ag_2S-NP) and silver chloride nanoparticles (AgCl-NP) at concentrations of 50 ng. L^{-1}. The experiments showed that, after an incubation time of 1 h, up to 70
% of the initial nanoparticle mass is dissolved. Though even after an incubation time of 3 days, a small amount of nanoparticles are still present. The coating and composition of the nanoparticles showed to have a major influence on the dissolution rate. CA@Ag-NPs were much slower dissolved than AgCl-NPs and Ag_2S-NPs due to the reducing effects of the citrate coating. Particle size distributions obtained by SP-ICP-MS measurements showed that large particles quickly partly dissolve to much smaller ones. TEM-EDX measurements showed that in case of in seawater incubated Ag_2S-NP the ratio Ag/S of initial 2:1 decreases to 1:1, which indicates that silver in contrast to sulfur is dissolved, while the latter is concentrating around the particles.

Keywords: silver nanoparticles, seawater, stability, cloud point extraction, TEM, EDX, SP-ICP-MS

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TP-35 Asymmetric flow field-flow fractionation (AF4) ICP-MS studies of the sorption of lead on nanoplastics

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Nanoplastics (particle size range from 1 to 1000 nm) are unintentionally produced, *i.e.,* from the degradation and the manufacturing of plastic objects [1]. They present a colloidal behavior and their nano-metric size makes them a potential efficient vector of many pollutants, including metals present in aquatic environment. This phenomenon has been poorly studied so far although is expected to significantly modify the environmental cycle of heavy metals.

An analytical strategy based on asymmetric flow field-flow fractionation (AF4) coupled to inductively coupled plasma mass spectrometry (ICP-MS) enabling a rapid detection of the presence of metals in several submicron populations in an unknown sample was developed. It was validated by an electrochemical method employing an *in-situ* polarography method. In a model study focused on lead, two batches of nanoplastics produced (Cordouan Technologies, Pessac, FR) from mechanical fragmentation of: (i) industrial polystyrene pellets and (ii) micro-plastics collected on a beach exposed to the North Atlantic Gyre were investigated. The adsorption kinetics of lead, isotherm and pH-edge were established highlighting the significant adsorption of Pb^{2+} onto nanoplastics.

The results show that Pb^{2+} adsorption kinetics is controlled by chemical reactions with the nanoplastics surface and to a lesser extent by intraparticle diffusion. The adsorption isotherm modelling using Freundlich model demonstrated that nanoplastics are strong adsorbents equivalent to hydrous ferric oxides such as ferrihydrite. The adsorption is highly dependent on pH probably in response to the adsorption of Pb^{2+} to oxygenated binding sites coming from the oxidation of the particles surface by UV under environmental conditions. These results seem to confirm that nanoplastics are efficient metal vector in the environment.

Keywords: nanoplastic, AF4, ICP-MS, metal adsorption

References

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TP-36 Application of seaFAST-pico system and SF-ICP- MS for determination of uranium concentration and its isotopic ratios in seawater

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Precise determination of the concentration and isotopic ratios of uranium are required in nuclear safeguards and forensic studies, as well in environmental monitoring. In addition to analysis of natural uranium isotopes, determination of ^{236}U is often of particular interest as its presence in environmental samples represents a good indication that nuclear material had been handled in the proximity. Recently, the determination of ^{236}U in addition to Pu isotopic analysis was recognized by International Atomic Energy Agency (IAEA) as an important signature to differentiate types of sources of contamination. However, the determination of ^{236}U is extremely difficult, because very low ^{236}U quantities must be measured in the presence of a large excess of ^{238}U and ^{235}U causing severe sources of interference in mass spectrometric and radiometric determinations.

The aim of this work was to provide simplified methodology for monitoring of uranium isotopic ratios in seawater samples. The proposed methodology for uranium isotopic quantification was based on performing two measurement cycles (A and B); at first (A-cycle) $^{235}U/^{238}U$ isotopic ratio was determined at low concentration (1 ppb ^{238}U), and then at second (B-cycle) $^{234}U/^{235}U$ and $^{236}U/^{235}U$ were determined at rather elevated U concentration (samples and standards contained up to 200 ppb ^{238}U). In both cycles, the intensities at six atomic masses were measured simultaneously; 233, 234, 235, 237, 238, 239 (A-cycle) or 232, 233, 234, 235, 236, 237 (B-cycle).

The developed procedure was based on chromatographic preconcentration (seaFAST-pico system) and measurements performed by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS). The merits of proposed methodology were: high sensitivity, good accuracy of isotopic measurements, relatively simple sample preparation procedure and potential for its application for U isotopic ratios analysis in any environmental samples.

The method was validated by determination of U isotopic ratios in a few reference materials certified for their isotopic composition (IRMM-184, IRMM-187, IRMM-3186). Additionally, two seawater samples from the Irish (IAEA-443) and the Mediterranean Sea were analyzed. The important factors (instrumental background, procedural blank, memory effect, peak tailing, mass bias, dead time, and hydride interferences) affecting isotopic ratio results and their final expanded uncertainties were checked during the validation process. In case of $^{236}U/^{235}U$ SF-ICP-MS analysis, the crucial factors influencing its detection capability and measurement accuracy were: (i) ^{236}U signal intensity; (ii) hydride formation $^{235}U^{1}H$; and (iii) peak tailing of ^{238}U on mass ^{236}U (abundance sensitivity). Total U concentrations in seawater samples were determined by the IDMS approach.

Keywords: SF-ICP-MS, uranium, isotopic ratios, seawater

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TP-37 Development of analytical procedure for determination of lanthanides at ng.L^{-1} level in mineral waters

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Owing to the fact that only precise determination of lanthanides in ground waters could allow understanding the hydrogeochemistry of groundwater flow systems, mixing processes and water-rock interaction, the goal of this work was to provide an appropriate analytical method for quantification of ultralow concentrations of lanthanides in mineral waters. The potential of the proposed methodology was demonstrated by analysis of the mineral water samples used for drinking and therapeutic purposes in Poland.

Accurate and precise quantification of lanthanides in mineral waters remains a difficult analytical task due to: very low elements concentrations (typically ng.L^{-1} level), high risk of contamination during sampling, and diverse and complex chemical matrices. The chemical composition of mineral waters depends on many synergistic natural factors: geological, hydrogeological, climatic and biological. The ground waters can contain more than 60 elements present in different concentrations and forms. The high content of dissolved solids (> 1% TDS), gaseous hydrocarbons, carbon, sulphur and nitrogen dioxides, hydrogen sulphide and methane, make such waters challenging objects for trace elements determination. Direct measurements of lanthanides in the mineral waters by inductively coupled plasma mass spectrometry (ICP-MS) are often hampered by the complex matrix that may cause significant spectral and non-spectral interferences (signal suppression or enhancement). With the aim to overcome the problems related to the influence of the chemical matrices present in the mineral waters, a sample pre-treatment step (analytes pre-concentration and matrix removal) has been proposed. In this study, an automated off- line seaFAST pre-concentration system with integrated columns containing chelating resin was applied in the sample pre-treatment step. The 10-fold pre-concentrated sample fraction was analyzed by ICP-MS and the amounts of lanthanides were determined applying the external standard calibration approach.

The proposed method was validated according to the ISO/IEC-17025 Standard and the Eurachem Guide (The Fitness for Purpose of Analytical Methods). The selectivity, linearity, working range of the calibration curve, limit of detection, repeatability and intermediate precision, as well as recovery and trueness were systematically assessed. In addition, the contributions of the individual analytical parameters to the final expanded uncertainty of the result were estimated, and the traceability of the measurements results was demonstrated.

Keywords: ICP-MS, method validation, sample preparation, lanthanides, mineral waters

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TP-38 Fast and high throughput digestion method for soil and sediment analysis using a modified graphite digestion system

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Since 2016, the prevention and control of soil pollution in agricultural land has attracted a lot of attention from the Chinese government. The government began a National Soil Pollution Survey for the agricultural land in 2017. Nationwide in China, about 1.35 million km^2 of farmland is included in the Soil Pollution Survey, which means that large numbers of soil and sediment samples need to be analyzed in a short period. The fast, sensitive, multi-element capabilities of ICP- MS make it an ideal analytical technique for measuring the soil and sediment samples required for the survey. However, to meet the analytical challenges, the sample preparation stage also needs to be efficient.

A fast and high throughput sample preparation method has been developed by modifying a graphite digestion system as follows: (i) the digestion tube size was redesigned to improve the digestion efficiency, (ii) two types of novel digestion tube cap were developed to optimize the accuracy and reproducibility of measurements, (iii) the digestion process (*e.g.* multi-acid ratio, heating program) was optimized to shorten the total digestion time.

This method was verified by analyzing eight soil and sediment CRMs sourced from five crop planting regions. Conventional acid digestion of soils and sediments by open-vessel, hotplate or closed-vessel digestion are very time-consuming and are prone to contamination and loss of volatiles. In comparison, the digestion approach described in this study could be used for the complete digestion of batches of over 200 samples in 4.5 hours.

Keywords: ICP-MS, soil and sediment, graphite digestion

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TP-39 Calibration for space-resolved laser ablation ICP-MS of tree rings

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The determination of elemental concentrations in annual rings provides the opportunity to detect long-term trends in nutrients affected by soil acidification (Ca, Mg, Al, etc.) or other changes in ecosystem conditions. In particular, phosphorous (P) is a unique indicator of the environmental long-term changes. Short-term effects were also investigated, such as effects of mast years, seasonal variability or efficiency of a fertilization or liming campaign. Negative trends in P levels in leaf- mirror readings from permanent observation plots suggested that P-nutrition in Europe has deteriorated significantly over the past 2-3 decades.

The analytical method of choice for this study was laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), due to the sensitive detection in spatial resolution of 10-100 µm. Self-prepared matrix-matched calibration standards were validated and used for different wood species, such as beech and spruce. The reference measurements showed an insignificant drift over the entire measurement period of months. This indicates the robustness and reliability of the measuring methodology. Clear tendencies and trends of the elemental contents in the tree rings could be shown.

However, small differences in the elemental concentrations due to the variation in density and structures of the artificial pressed wood calibration standards compared to grown wood samples were monitored. Digested wood samples showed slightly higher elemental concentrations. In addition, minor variations within late wood and early wood and the different wood species itself, due to different ablation rates, could be observed. To overcome the influence of the different wood density and the self-made calibration standards, the strategy of on-line addition of standard solution and laser ablation will be shown in this poster.

Keywords: tree rings, wood, phosphorus, on, line standard addition, LA-ICP-MS

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TP-40 Silver nanoparticles in natural water bodies - is it only humans who are to blame?

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Nanotechnology is a heavily emerging field due to a variety of applications for different nanomaterials. For instance, nanoparticulate rhodium is used in car exhaust catalysts, titanium dioxide nanoparticles are effective UV radiation absorbers in sunscreen and silver nanoparticles (Ag-NPs) are present in antimicrobial applications for fabrics, cosmetics and sterile surfaces in hospitals. Usage and disposal of these products finally lead to a release of nanoparticles in the environment primarily via wastewater streams. Wastewater treatment plants (WWTPs) serve as kind of distributors for nanomaterials into the environment like rivers and lakes. Developing nanotechnology and its applications requires a simultaneous improvement of analytical techniques and instruments to determine nanomaterials in environmental samples for a proper risk assessment.

However, detection and quantification of nanomaterials of anthropogenic origin in environmental samples is a major challenge for environmental monitoring of nanomaterials. Complex matrices, interference by non-particulate species and low concentrations of nanomaterials are some of the challenges, which need sophisticated analytical solutions.

Cloud point extraction (CPE) is a very helpful tool as it allows a species selective extraction of nanoparticles from complex matrices into a surfactant rich phase even in presence of dissolved species. CPE is a simple and fast surfactant mediated operation, which can be performed in virtually every laboratory. High enrichment factors around 100 from initial volumes of 40 ml are possible and the extracted particles are not modified by the CPE procedure with respect to their shape and composition.

Ag-NPs, which are suspected to pose a particular risk to aquatic microorganisms, can be selectively enriched by CPE and detected with electrothermal atomic absorption spectrometry (ETAAS) or inductively coupled plasma mass spectrometry (ICP-MS) with detection limits as low as 0.2 $ng.L^{-1}$. In combination with single particle ICP-MS (SP-ICP-MS), size-selective measurements with a detection limit of 0.25 $ng.L^{-1}$ for particles with a size down to 10 nm can also be performed paving a way for a more comprehensive understanding of the formation and distribution of Ag-b-NPs in the environment. Coupling CPE to SP-ICP-MS contributes significantly to the improvement of the minimum detectable particle size. Signal background caused by dissolved element species cover small particles' signals in the SP-ICP-MS spectra. By removing these dissolved species prior to the measurement, the detection of very small particles in environmental samples is possible now.

Applying the presented method, we were able to measure the concentration of Ag-NPs along a river from its source to its estuary addressing the effect of WWTPs located next to the river. Moreover, the natural formation of Ag-NPs from geogenic silver sources in lakes was studied. Ag- NPs found in environmental samples are not only of anthropogenic origin – on the contrary, Ag-NPs seem to be present at a geogenic background level even in lakes without any anthropogenic input.

Keywords: silver nanoparticles, cloud point extraction, SP-ICP-MS, real environmental monitoring

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TP-41 Determination of ^{239}Pu, ^{240}Pu concentration and $^{240}Pu/^{239}Pu$ atom ratio in seawater using an isotope dilution sector field-inductively coupled plasma-mass spectrometry

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The plutonium isotopes, ^{239}Pu and ^{240}Pu, have been added to the surface ocean mainly as a consequence of global fallout from atmospheric nuclear weapons testing, while a second source has been close-in fallout from nuclear weapons testing at the Pacific Proving Grounds. Since the $^{240}Pu/^{239}Pu$ atom ratio depends on the specific weapons design and test yield, it is a powerful fingerprint to identify the sources of Pu in the ocean. The objectives of this study are to determine the ^{239}Pu, ^{240}Pu and ^{239}Pu + ^{240}Pu concentrations, and $^{240}Pu/^{239}Pu$ atom ratios in seawater from the Indian Ocean and to discuss the transport processes of plutonium in the ocean. The ^{239}Pu and ^{240}Pu concentrations and $^{240}Pu/^{239}Pu$ atom ratios were measured with an isotope dilution sector field- inductively coupled plasma-mass spectrometer, which was equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. The atom ratios in water column from the Indian Ocean were significantly higher than the mean global fallout ratio of
0.180. These high atom ratios proved the existence of close-in fallout plutonium originating from the Pacific Proving Grounds. The Bikini close-in tropospheric fallout Pu could be transported to the eastern Indian Ocean by ocean currents.

Keywords: $^{240}Pu/^{239}Pu$ atom ratio, sector field inductively coupled plasma mass spectrometry, seawater, Isotope dilution

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TP-42 Assessment of heavy metals in surficial marine sediments from the Lebanese coast (Eastern Mediterranean)

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The increased urbanization and industrialization along the Lebanese coast (Eastern Mediterranean) represent the main sources of pollution in the country. The presence of uncontrolled solid waste open-air dumpsites along the coast in addition to the discharge of domestic and industrial effluents into the sea without prior treatment affect the quality of the coastal marine environment and threaten the survival of many marine species. In Beirut area, Costa Brava is an open-air dumpsite receiving solid waste since 1998. It is situated 167 meters away from the International Airport and is located next to the Ghadir primary treatment wastewater plant. The aim of the present study was to assess the contamination status of the marine environment next to the Costa Brava dumpsite by determining the levels of heavy metals and trace elements (Li, Ti, V, Fe, Ge, As, Se, Te, Sr, Ba, Cs, Cd, Tl, Pb, Th and U) in sediments collected between January 2014 and October 2018. Metals were analyzed using inductively coupled plasma mass spectrometry (ICP- CRC-MS, 7700 Agilent). The results of the present study show that sediments in some sampling points are impacted by heavy metals and trace elements.

Keywords: heavy metals, trace elements, ICP-MS, sediments, marine pollution, Lebanon.

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TP-43 "Bulk and trace elements" in saline water produced from the Danish North Sea: The chemical analysis and the trends in the retrieved data

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When oil is produced from a well a varying amount of highly saline water from the subsurface is produced along with the petroleum fluid. The ions Na^+, Mg^{2+}, Ca^{2+} and K^+ are present in the produced water in concentrations most often above 100 ppm. Hence, these are classified as bulk ions. Ba^{2+} and Sr^{2+} are present in sub-ppm concentrations and are, thus, considered trace ions along with other metal species present at ppb levels. All six elements are analyzed by a multi-step analytical procedure designed for high saline multi-component mixtures such as sea water and further optimized for petroleum fluids employing an inductively coupled plasma - optical emission spectrometer (ICP-OES) instrument. Due to the complex composition and wide range in concentrations found in these samples, this analysis is challenging: The choice of sample preparation, dilution factor(s), internal standard(s) and the complex matrix effects in these natural samples are presented and discussed. Produced water also contains organic material, Cl^- and SO_4^{2-}, which we analyze using ion chromatography (IC) and HR-LC-MS. From historical data, we obtain the composition of the produced water and the changes in concentration over time indicating the complex mixing of formation water and injected seawater. Further details in the observed trends in this data are presented and interpreted from a geochemical perspective

Keywords: ICP, OES, produced water, sample preparation, matrix effects, multi, component analysis

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TP-44 Rapid analysis of Rare Earth Elements in freshwater by ICP-MS with online preconcentration

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The use of Rare Earth Elements (REEs) for a wide range of applications (electronics, catalysts, medical imaging...) is growing. This anthropogenic use can induce some enrichments of REEs compared to their natural abundance. The aim of the ECOTREE project (Ecotoxicology of Rare Earth Elements in Aquatic Systems) is to evaluate the ecotoxicity of REEs in freshwater, related with their dynamic and speciation. To that end, a monitoring of REEs by ICP-MS was required.

However, as most of REEs concentrations still remain very low in freshwater, the values measured by direct analysis in ICP-MS are often under Limits of Quantification (LOQs). In order to increase the sensitivity of the method, a preconcentration step was required. Among the methods described in literature, Solid Phase Extraction was chosen as the most suitable, with the use of a chelating resin, Toyopearl®-AF-Chelate-650M (Tosoh Bioscience). This resin has been reported in literature as a good chelating agent for REEs. In order to avoid a very long and tedious manual preparation process, an online preconcentration method was set up. The idea was to take advantage of the ISIS 3 system (Integrated Sample Introduction System) installed on our Agilent 7900 ICP- MS. The injection loop was replaced by a cartridge filled with the chelating resin. After being adjusted at pH 5.3, 40 mL of sample were adsorbed on the resin (loading step). Then, the cartridge was eluted with a carrier solution of 0.7M HNO_3 (injection step), and directly sent to nebulizer.

The LOQs ranged from 0.05 to 0.25 ng/L, and the calibration curves were linear up to 5 ng/L. Thulium was used as internal standard. The total duration of the method, including preconcentration, was around 12 min.

Keywords: rare Earth Elements, ICP, MS, freshwater, preconcentration

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TP-45 Screening of metals in surface and drinking waters using semi quantitative analysis ICP-MS.

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Water-link is a drinking water company, located in the Antwerp region, which provides drinking water for over 2 million people in Flanders and the Netherlands. Surface water, coming from the River Meuse and transported to the catchment areas of our production sites by the Albert Channel, is purified to drinking water with a quality according to the EC regulation 93/98/EU. However, there's a possibility companies located along the River Meuse and the Albert Channel river-banks pour their industrial waste water in the channel. Most environmental studies focus on certain metals e.g. Cd,Cr,Cu,Hg,Ni,Zn,Pb. New European drinking water legislation focusses more on the knowledge of all risks. Hence, getting a full view of all present metals, is extremely important. A routine method was optimized and results of a screening campaign regarding raw and drinking water started in Q3 2018 will be presented.

Keywords: environmental, screening

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TP-46 Bio-indication of traffic impact on forest ecosystems

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It its well accepted that traffic influences the surrounding ecosystems. The road boundtraffic increased by 13 % from 2011 to 2016. Therefore, we identified characteristic contaminants and determined their concentrations in suitable sample matrices to assess the dynamics of their movement in the environment.

In this work, a spruce (Norway spruce - *Picea abies*) and a pine forest (Scots pine - *Pinus sylvestris*), were chosen as the model ecosystems. The spruce forest is located in the Bohemian- Moravian highlands, directly next to highway D1 connecting Prague and Brno ¿ 126100 km from Prague. This locality is constantly exposed to road traffic (¿ 12641000 vehicles per day, v/d). The pine forest is located between Prague and Mladá Boleslav and is mutually influenced by three different types of traffic intensities. The traffic situations were as follows: directly next to highway D10 (¿ 12637000 v/d), a 1st class road (¿ 1263000 v/d) and a background locality (< 2000 v/d). Samples collected and analyzed include soil, spruce/pine needles of different age (one, two and three plus years old), forest grass, and moss in different distances from the respective roads.

Soil samples were prepared according ISO 11466 (Soil quality – Extraction of trace elements soluble in *aqua regia*). Dried needles, forest grass, and moss were crushed, milled and digested with nitric acid using microwave heating. Concentrations of 20 elements were determined with an ICPMS/MS (Agilent 8800 ICP-QQQ, Agilent Technologies, Japan). Data were evaluated for the two different types of forests in the context of traffic loading, to interpret the complex interaction patterns between roads and surrounding ecosystems. The poster discusses the highlights of the study.

Keywords: bioindication, ICPMS/MS, traffic, spruce/pine needles

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TP-47 Evaluation of Lead in Drinking Water in Daycare Centres

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Human exposure to lead is usually assessed through the measurement of lead in blood. In the Canadian population, lead exposure and blood lead levels (BLL) have significantly decreased since the phase out of leaded gasoline in 1993. Recent studies show that BLL

Today, one of the major sources of environmental exposure to lead is drinking water, which can contribute to 10-20% of lead exposure in children and adults and 40-60% in infants. Most lead in drinking water arises from plumbing systems in buildings rather than source water. The existing Canadian drinking water guideline states the Maximum Acceptable Concentration (MAC) as 10 µg/ L total lead (last updated in 1992) [1]. Considering the health concerns in children, however, recently a MAC of 5 µg/L has been proposed and it is noted that every effort should be made to maintain lead levels in drinking water as low as reasonably achievable (Health Canada, 2017).

Following the recent growing concerns related to lead contamination of drinking water and the health concerns for infants and young children, a study was conducted to investigate the levels of lead at 150 daycares in Alberta, Canada. Samples (n=1431) were collected from all cold taps and fountains that were regularly used for drinking or food preparation using Random Daytime (RDT) sampling and without flushing.

Sample preparation followed the Environmental Protection Agency (EPA) 200.8 where samples were acidified with nitric acid (HNO_3, 1% v/v) and analyzed using Agilent 7700 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The limit of quantification was 0.1 µg/ L.

The concentration of lead ranged from not detected (< 0.1 µg/L) to 35.5 µg/L. Lead was detected in about 80% of the tested samples, however, the majority of these samples had lead concentration below the current MAC (10 µg/L) and the proposed MAC (5 µg/L). Lead concentration was above 5 µg/L in 37 samples (2.6%) and above 10 µg/L in 9 samples (0.6%). In certain locations, it was observed that lead concentration varied at different taps in the same building. This study demonstrates low levels of lead in drinking water at daycare centres in Alberta and shows that testing every tap in a building is important in order to evaluate lead exposure and to choose an appropriate mitigation strategy.

Final Human Health State of the Science Report on Lead, Health Canada (2013)

Keywords: lead, drinking water

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TP-48 Microwave-assisted Acid Digestion of Cannabis Product

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Cannabis, one of the earliest cultivated plants, originates from central Asia or northern parts of south Asia. Being quite robust, the plant has since not only been used as medicine, but also for food-, textile-, and many other industries. Starting in the 19th century the significance of cannabis as medication increased considerably having shown beneficial effects in the treatment of pain, mood disorders, and inflammatory diseases. In the last decades the prohibition of cannabis has been scrutinized and meanwhile sanctioned for medical use in Germany, the Netherlands, the Czech Republic, the UK, Israel and in some US states. Uruguay, Canada and Georgia are the first countries to already fully legalize the use of cannabis.

Since most of the final products of cannabis are designed for human consumption, cannabis- based products such as oral medications, edibles, oils, tinctures and salves as well as the plants and plant materials itself must therefore be tested for the presence of heavy metals and other elements to ensure consumer safety and product quality.

In order to demonstrate the suitability of HVT vessels with SMART VENT technology for sample preparation of cannabis prior to element analysis the recovery rates of spiked samples (Be, Ti, V, Cr, Co, Ni, As, Se, Mo, Ag, Cd, Hq, Sn, Sb, Cs, La, Ce, Nd, Sm, Eu, Dy, Gd, Ho, Er, Lu, Hg, Tl, Pb, Th, and U) were determined. After the microwave assisted digestion the solutions were measured with an ICP-MS system equipped with a micromist nebulizer and a Peltier cooled spray chamber. The results are presented in relation to the classification mentioned in the respective chapters of USP , Ph. Eur. 5.20 and ICH Q3D.

Keywords: digestion, microwave assisted digestion, cannabis

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TP-49 ICP OES and LIBS approaches for the analysis of nickeliferous minerals

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Cuban nickel deposits are one of the biggest in the world with, approximately, 37% of the planet reserves. The processing and extraction of nickel have prevailed since 1941. Nowadays, the nickel industry is an important sector of the Cuban economy. In this context, the present study was aimed at the increment of the analytical capacities for the multielemental analysis of nickeliferous minerals. Based on the Inductively coupled plasma optical emission spectrometry (ICP OES), the quantification of Al, Ca, Co, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, P, and Zn was achieved with trueness and precision around 100% and lower than 10%, respectively. Samples were, previously, subjected to microwave-assisted acid digestion procedure. Novel matrix effect characteristics in laterite (Al+Cr+Fe+Ni) and serpentine (Mg+Fe+Ni) were described during the analytical study. The selection of robust plasma conditions in combination with the use of matrix-matching calibration standards overcame the matrix effect. In a second step, the major elements Al, Cr, Fe, Mg, Mn, and Ni were quantified by Laser-induced breakdown spectrometry (LIBS) with relative errors between
0.09 and 6%. A novel sample preparation is proposed, that includes the formation of a sample slurry and, then its immobilization in a polyvinyl alcohol (PVA) polymer film. In addition, the Multi- energy calibration (MEC) procedure was applied for the first time in the LIBS analysis of solid samples. Nickel and Cr were quantified in nickeliferous minerals with precision between 6 and 9% and good agreement with reference concentrations. LIBS in combination with MEC and/or immobilization of sample slurry in a polymer film represent effective approaches to improve the analysis of solid samples with complex and variable matrix composition, reducing waste generation, analysis time and is in accordance with Green Chemistry principles. In summary, the high potential of ICP OES for the multielemental analysis of samples with complex composition is confirmed, while new alternative methods are proposed using LIBS. The authors are grateful to CNPq (processes 401074/2015-4 and 305637/2015-0), and Fapesp (2016/01513-0). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. This study was performed in the frame of the International Cooperation Program of the Universidad Complutense de Madrid and Universidad de la Habana; and also as part of the IMRE Project "Improvement of the reliability of the analysis of environmental samples and advanced materials

Keywords: nickeliferous minerals, ICP OES, LIBS, sample preparation, multienergy calibration

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TP-50 Analytical issues for the characterization of nanomaterials in consumer products for regulatory purposes.

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The emergence of new applications based on the use of nanomaterials in the food sector is as much a source of interest for technical innovation, as it is a source of concern for consumers.

In Europe, food products containing manufactured nanomaterials are subject to a labeling obligation in order to protect and inform consumers. In this context, the French fraud regulatory agency (DGCCRF) has been carrying out controls to look for the presence of nano ingredients in food products since 2017.

However, the characterization of nanomaterials remains an analytical challenge due to the interactions of nanoparticles with various matrix constituents, the sensitivity required for measurements and the size polydispersity related to the state of aggregation / agglomeration / dissolution of the particles to be measured.

A simple and reproducible sample preparation procedure based on water dispersion followed by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) analysis has therefore been developed and applied to characterize titanium dioxide particle size distribution (PSD) in various food products (different types of candies, white sauce etc.) and their corresponding food-grade additives (E171). The developed SP-ICP-MS procedure relies on the combination of $^{47}TiO_2$ and $^{48}TiO_2$ PSDs in order to better account for the polydispersity of food-grade TiO_2. Electron microscopy was used throughout the development steps to confirm and validate SP-ICP-MS particle size measurements. The performance of the preparation procedure was demonstrated by comparing the TiO_2 PSDs obtained for the food products and for their corresponding pure additives. The very good agreement obtained has allowed validation of size measurements. The PSD found for TiO_2 in the different studied food products was in the range of 110 – 240 nm with a percentage of particles presenting a particle size below 100 nm ranging from 4 to 40 %.

Keywords: nanomaterial, food, titanium dioxide, size measurements, single particle inductively coupled plasma mass spectrometry, Electron microscopy

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TP-51 Determination of nanopowders using MIP-OES operating in a single particle mode

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In the last twenty years there has been a rapid increase in the development, production and application of engineered nanomaterials, including metallic NPs, metal oxide NPs and more advanced semiconductor nanomaterials. Thus, material science requires advanced analytical methods which allow size-fractionated and chemical quantification of powdered nanomaterials. Without a doubt, single-particle inductively coupled plasma mass spectrometry is an emerging analytical technique that can determine NPs dispersions **[1]**. In parallel, single particle microwave plasma optical emission spectrometry (SP-MWP-OES) is considered as a promising approach for detection and sizing of nanopowders, providing information about their elemental composition, size, dispersity, agglomeration and aggregation of NPs.

It is noteworthy that some nanomaterials are available and applicable in powder form, but not in suspensions or colloids. In spite of the availability of a number of techniques for size and particle number measurements (TEM, AFM, DLS), the characterization of nanopowders is challenging. The SP-MWP-OES is a real-time fast detection technique that allows capture of the light radiation events occurring when individual NPs are atomized and excited in the plasma, which is related to information such as particle count, size distribution and stoichiometry. A sample introduction system based on pneumatic nebulization which allows the transportation of single NPs into the plasma was used. MWP-OES can measure both metals and nonmetals in a short time, and elemental constituents of NPs would be detected with high sensitivity. Thus, NPs can be characterized by the corresponding element-to-element molar ratios and compared to the theoretically expected values.

This paper mainly addresses the measurement method which has been developed and established for NPs size and size distribution measurements at the Warsaw University of Technology **[2]**. In this work, the feasibility of SP-MWP-OES is investigated for providing detailed information on small particles below 50 nm at integration times as short as 4-10 ms. Quantitative data were collected for the size-based speciation of the investigated nanopowders. Size LODs of about 10 nm for MgO, In_2O_3 and ZnO were achieved for an integration time of 10 ms. At present, SP-MWP-OES cannot still be considered as a mature methodology, however, it shows great potential as a simple rapid selective method in nanopowder research due to high sensitivity, low consumption of sample material, high sample transport efficiency, temporally separated signals of single events corresponding to one particle and possibility of calibrating the nanoparticle mass by using standard nanomaterials. The calibration work will be further extended in the future to also cover more complex nanoparticle samples concerning their shape characteristics and size distributions.

Keywords: single partcile measurements, microwave plasma, optical emission spectrometry

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TP-52 Analytical monitoring of biological synthesis selenium nanoparticles using PCVG-MIP-OES and UV- Vis spectrophotometry and their further application as a mercury detoxifying agent

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Selenium is well known as an essential constituent of antioxidant enzymes, potential antagonist for the uptake of mercury and chemopreventive agent **[1]**. Selenium nanoparticles (Se- NPs) are increasingly recognized as a potential source of the element for organisms being an alternative to common forms of selenium. It is noteworthy that the toxicity of selenide (SeII), selenite (SeIV) or selenate (SeVI) is definitely higher than the toxicity for elemental selenium of nano size **[2,3]**. Moreover, Se-NPs exhibit higher bioavailability than both inorganic Se and selenium containing amino acids **[4]**. The application of SeNPs in biological systems can be restricted due to the presence of toxic concomitants in the reaction medium including selenium precursor and reducing or stabilizing agents.

The aim of this study was the optimization of biological Se-NPs synthesis using yeast as a green "reductants" for ionic Se and the development of green analytical procedure suitable for direct monitoring of Se-NPs synthesis. Additionally, the Se-NPs produced by non-toxic reagent were characterized and the yield of the reaction was determined. Moreover, mercury-antagonistic properties of Se-NPs were examined using PCVG-SPME-MIP-OES.

Biological Se-NPs synthesis using yeast *Saccharomyces boulardii* have been successfully monitored using both continuous photochemical vapor generation (PCVG) coupled with MIP-OES and UV-Vis spectrophotometry. PCVG-MIP-OES allows for fast and selective determination of unreacted selenite in the presence of Se-NPs and matrix components, enabling accurate calculation of the yield of the Se-NPs synthesis. For the analysis, these analyte ions were converted into volatile species by UV irradiation of their aqueous solution in the presence of 15% v/v acetic acid. The UV- Vis spectrum of the resulting nanoparticle solution displayed the SPR bands at 561 and 654 nm confirming the presence of Se-NPs. Furthermore, Se-NPs were successfully applied in the process of detoxification of inorganic mercury.

Keywords: selenium nanoparticles synthesis, green chemistry, analytical monitoring, photochemical vapor generation, optical emission spectrometry, UV-Vis spectrophotometry

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TP-53 Automated solution for processing complex data sets generated in single particle and single cell analysis by ICP-TOF-MS

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The main advantage of inductively coupled plasma time of flight mass spectrometry (ICP- TOF-MS) in respect to the analysis of individual particles and cells is the capability of simultaneous detection of the entire range of elements. It enables *e.g.* single particle fingerprinting to identify small quantities of engineered nanoparticles in natural systems **[1,2]** or uncompromised detection of endogenous and toxic elements in every individual cell. The icpTOF (TOFWERK, Thun) can acquire a complete mass spectrum at the sampling rate of a few tens of kHz. This ensures comprehensive and unbiased representation of the sample, but poses some challenges to data post-processing due to large information density. In this contribution, we present an automated software solution for multi-element sample screening, particle/cell thresholding and quantification. A screening workflow was designed to identify and report all elements present in form of particulates and their potential correlations (*e.g.* how many particles contain both Al and Ti), which is particularly useful for unknown systems. We describe an algorithm the software applies for separating particle signals from the signal of the ionic fraction of the corresponding analyte or instrumental noise. Corrected signals of particles and cells in counts and the signals of ionic background are stored together with the precise time stamps that also serve as indicators for retention times, as required for coupling with field flow fractionation techniques. Finally, we will show how particle/cell counts are converted to element mass and particulate size (whenever feasible) based on the method proposed by Pace *et al.* **[3]**, when the quantification workflow is performed.

Keywords: ICP-TOF-MS, single nanoparticles, single cells, post, processing

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TP-54 Study of the ion cloud profiles from gold and silver nanoparticles in ICP-MS

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As the number of nanoparticle applications in technology, medicine, and consumer products increases, there is also growing interest in the precise characterization of engineered nanoparticles. Gold and silver nanoparticles have been of special interest in imaging and sensing applications, due to their unique optical traits arising from the localized surface plasmon resonance. The combination of these elements, in the form of core-shell nanoparticles, brings together the beneficial effects of both particles. To further tune the particle properties, it is crucial to optimise the reaction conditions, which can be achieved by a comprehensive yet fast analysis of the particle number concentration, size and composition of the reaction mixture.

Established techniques for nanoparticle characterization, such as UV-VIS spectroscopy or transmission electron microscopy, either lack the specific look at a single particle itself, call for time consuming sample preparation or provide only basic information on particle number concentrations. This gap can be filled by utilizing single particle ICP-MS (SP-ICP-MS) techniques for the analysis of nanoparticle reaction mixtures with fast data acquisition rates down to the microsecond range.

This study shows the influence of the particle diameter on the extension of the formed ion clouds by introducing precisely sized gold nanoparticles with diameters from 15 to 100 nm in SP- ICP-MS. Furthermore, the ion cloud generation was computationally modelled to get deeper insight into the signal generation. The implications of this work are transferred to the SP-ICP-MS analysis of silver nanoparticles and, eventually, the analysis of bimetallic nanoparticles and aggregates.

Keywords: single particle ICP-MS, nanoparticle, gold, silver,

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TP-55 Contribution to SP-ICP-MS accurate spherical gold nanoparticles size determination: a comparison with small angle X-ray scattering

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Small angle X-rays scattering spectroscopy (SAXS) is the method of choice for nanoparticle diameter and concentration determination. It is metrologically traceable for spherical nanoparticle mean diameter determination and does not require any sample preparation or calibration. On the other hand, single particle ICP-MS (SP-ICP-MS) is still under developments and requires involved process clarification and accuracy improvement.

The strategy of this presentation based on 6 spherical gold nanoparticle suspensions distributed over a large size range (30, 50, 60, 80, 100 and150 nm), is the comparison of the two techniques to study comprehensively SP-ICP-MS performance and observe phenomena. Potential matrix effects are eliminated by stabilizing nanoparticles with chitosan in HCL. Chitosan encapsulates nanoparticles, stabilizes their dispersion and protects them from dissolution. Detection counting/analog threshold and timeout appear as the relevant parameters for transient signals. They show an influence not only on mean signal but also on signal distribution. The detection tuning proposed allow to linearly calibrate the nanoparticle distribution signal to cubed diameter over the entire range studied with no sensitivity diminution. Comparing the 3 classical transport efficiency methods (number, size and waste), size transport efficiency is shown as the most accurate.

A procedure is proposed, it is validated analyzing three gold nanoparticles suspensions (135, 40 and 50 nm). The results are consistent with SAXS measurements.

Keywords: SP-IC-PMS, SAXS, single nanoparticle, colloid stabilization, chitosan

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TP-56 Single particle ICP-MS as screening method for detection of nanoparticles

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a feasible methodology for the measurement of nanoparticles, providing information about their number concentration and size distributions, at mass concentration levels down to the ng.L^{-1}. SP-ICP-MS has been considered as a suitable methodology for screening analysis of samples containing nanoparticles by a number of authors, although a complete metrological treatment of SP-ICP-MS as screening method, including its validation has not been performed. The use of SP-ICP-MS as screening method for detection of nanoparticles in a sample should just answer the question of whether there are nanoparticles in that sample. Whereas identification of a conventional analyte involves just to know its chemical composition, in the case of a nanoparticle, apart from its composition, information related to the size is also required.

SP-ICP-MS is a counting technique and their measurements are performed at high acquisition frequencies (> 100 Hz) during short periods of time (minutes), obtaining time scans consisting of a baseline and a number of pulses produce by the particles themselves. The main step for identifying particles in a time scan involves the discrimination between readings from particles and from the baseline and it should involve to consider certain threshold value. Threshold criteria for removing the continuous contributions were studied on the basis of the estimation of the critical value for baseline distributions adapted from the treatment of detection developed by Currie **[1]**. This critical value is defined as the response of the instrument above which an observed signal is reliably attributed to the presence of the analyte. Threshold criteria were studied based on reducing the occurrence of false positives, without negatively affecting number concentration detection limits.

The objectives of this work are the evaluation and validation SP-ICP-MS as screening method for detection of nanoparticles in suspensions by applying metrological criteria and concepts related to detectability in SP-ICP-MS. Application to different types of samples will be presented.

Keywords: single particle ICP-MS, nanomaterial, nanoparticle, screening, detection

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TP-57 Optimization and application of single particle ICP-MS to TiO_2 nanoparticles analysis in foodstuffs

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Titanium dioxide (TiO_2) is used as food additive (E171) in order to make products whiter and/or shiny. Since 2012, it has been demonstrated that TiO_2 in E171 can be partially present under nanoparticles (NPs) form. Despite the regulation imposing the reporting of nanoparticles presence in foodstuffs, it remains difficult for food analysis laboratories to accurately quantify the nanoparticle fraction in food products with common analytical approaches.

This study focuses on the development of liquid methods for TiO_2-NPs characterization in food, namely single particle approach with inductively coupled plasma mass spectrometry (SP-ICP- MS).

SP-ICP-MS approach for NPs characterisation is a recent and promising method that allows size measurement of particles without any upstream separation technique. In this study, several parameters have been optimised such as titanium isotope analysed according to matrix effect. The dwell time and the solvent chemical nature were also optimised. The signal background was decrease by self-aspiration mode of sampling. Moreover, the data treatment software has been compared with the data treatment with internal spreadsheet. Then, an extraction protocol of NPs has been developed from food products.

Finally, this optimised analytical method was applied to the analysis of several food products containing the E171 additive and allows obtaining an accurate size distribution of TiO_2- NPs containing in these samples. The size limit detection obtained with the isotope ^{48}Ti is around 25-30 nm.

Keywords: nanoparticles, titanium dioxide, foodstuffs, single particle, optimization

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TP-58 Synthesis and characterization of tellurium based nanoparticules through a multitechnique platform including hyphenated ICP-MS techniques

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Nanotechnology has been considered during the last years as a powerful tool to fight against the emerging problem of resistant bacterial infection. In this context, a wide range of metal and metal oxide nanoparticles such as Ag, Cu, ZnO, CuO or TiO_2 have been considered as alternative antimicrobial agents. Otherwise, less common nanoparticles such as selenium nanoparticles (Se- NPs) and tellurium based nanoparticles (Te-NPs) have focused the attention of researchers. The antimicrobial potential of nanoparticles is highly dependent on their physicochemical properties such as size, charge, surface morphology, aggregation state and crystal structure. Hence, a proper characterization of these nanoparticles prior to assessing their potential antimicrobial activity is of great importance. The complexity of nanoparticle characterization leads to the employment of multitechnique platform which combines spectroscopy techniques with light scattering and electron microscopy images. In this work, tellurium based nanoparticles (Te-NPs) have been synthesized and fully characterised through a multi-modal platform including electron transmission microscopy (TEM), dynamic light scattering (DLS), X-ray diffraction (RX), Fourier-transform infrared spectroscopy (FTIR) and asymmetrical flow-field flow fractionation (AF4) separation combined with inductively coupled plasma mass spectrometry (ICP-MS). Challenges and difficulties during AF4-ICP-MS characterization are further discussed. For this purpose, parameters affecting fractionation such as type of membrane, composition of mobile phase or flow-rates were fully optimized. Finally, antibiofilm potential of Te-NPs was assessed through common pathogen bacteria by using imaging techniques such as confocal microscopy.

Keywords: nanoparticles characterization, asymmetrical flow, field flow fractionation, ICP-MS, tellurium nanoparticles, antibiofilm potential

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TP-59 Challenges and solutions for measuring small sized nanoparticles

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In recent years, due to the need for impurity monitoring in the processing of materials and semiconductors, the demand for analysis of small-sized nanoparticles has become increasingly prominent. However, in the analysis of nanoparticles by single particle ICP-MS (SP-ICP-MS), there are some key factors that affect the size detection limit of nanoparticles in real samples.

When the particle size is reduced to 1/2, the particle mass decreases to 1/8 of the original. Therefore, higher sensitivity of ICP-MS and lower background are both needed when analyzing the smaller size nanoparticles. In this study, smaller size nanoparticles, such as 5 nm Au , are used as examples to investigate the relationship between the particle intensity and the ionic(tuning) intensity. With the combination of ultra-high sensitivity ICP-MS/MS and the analysis technology of the operator, SPICP-MS succeeded to analyze the 5 nm Au nanoparticles with the sizedistribution.

During the investigation, it was observed that the improvement in ionic state sensitivity is not always proportional to the improvement in particle sensitivity. However, if the ionic sensitivity is not improved, the particle sensitivity is difficult to improve.

In addition, the ionic concentration in the solution is also an important factor affecting the size detection limit. If the ionic concentration in the solution increases, it affects the small size measurement even if the particle sensitivity is high. This study demonstrates that parsing small- sized nanoparticles requires increasing sensitivity and reducing the importance of the background.

Keywords: ICP-MS/MS, SP-ICP-MS, Au nanoparticle, small sized nanoparticle analysis

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TP-60 Interaction of silver nanoparticules with agricultural soils: effects to size and chemical form

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Silver nanoparticles (Ag-NPs) are one of the most used engineered nanoparticles and their production has increased during last years. As a consequence, these particles inevitably enter into the environment reaching soils. Once in the soil, Ag-NPs can suffer different processes that affect their mobility, transport, bioavailability and fate. Therefore, knowledge of the processes that take place in this environmental compartment is of great importance **[1]**.

According to different studies, nanoparticles interaction with soils depends on soil properties (*e.g.* ion exchange capacity, conductivity and organic matter content) as well as on nanoparticles characteristics (mainly size, surface area and surface coating) **[2]**.

In this work, batch adsorption/desorption tests with 75 nm PVP coated Ag-NPs were performed using 5 Mediterranean agricultural soils with different physicochemical properties. To examine the mobility of the studied Ag-NPs and to determine if during the adsorption/desorption processes from soils, their size and nanoform are altered, water leachates were analysed first by ICP-OES, to quantify total silver amounts, and afterwards by single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) to ascertain their chemical form (Ag^+/Ag-NPs) and size (Ag-NPs). Water leaching tests, using different experimental conditions, indicated that Ag-NPs were strongly retained to soils, arising values of just 1% lixiviation for only one of the studied soils.

Our results also show that soil physicochemical properties are crucial to maintain the size and nanoform of the silver particles, being soils with high cation exchange capacity the ones that alters more the Ag-NPs present in the leaching solution. Ag-NP characteristics are also affected by the conditions used in the lixiviation process, such as drying temperature or sonication.

Keywords: silver nanoparticles, agricultural soils, nanoparticle size, lixiviation

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TP-61 Size characterization and speciation of gold and silver nanoparticles and their ionic counterparts by hydrodynamic chromatography coupled to ICP-MS

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The continuous advances in nanoscience involve the growing use of different engineered nanoparticles (ENPs) in an increasing number of consumer products. This fact requires the adaptation of existing techniques and methods or the development of new ones to monitor their occurrence, fate and transformations in different scenarios. Different techniques and methodological approaches for the characterization and quantification of ENPs and their derivatives in complex samples have been reviewed **[1]**. In order to understand the environmental impact or the toxicological mechanisms of inorganic ENPs, it is critical to discriminate among dissolved and particulate forms of the element involved.

Asymmetric flow field flow fractionation (AF4) and hydrodynamic chromatography (HDC) are commonly coupled to ICP-MS as element specific detector for the separation and determination of inorganic ENPs in a variety of samples. Comparing AF4 and HDC, although HDC is a robust and versatile separation technique, its resolving power is much lower than AF4. On the other hand, recoveries for HDC are on average better than for AF4. An additional advantage of HDC over AF4 lies in the analysis time, which can be reduced to less than 10 minutes in comparison with 30-45 minutes of AF4. Moreover, dissolved low molecular mass species are not lost in HDC as in AF4, due to the ultrafiltration membranes used in its separation channel. Thus HDC-ICP-MS can provide simultaneous information about dissolved and particulate species of an element in less than about ten minutes, which is not the case of AF4.

The aim of this study is to systematically investigate and evaluate the influence of the main HDC parameters (mobile phase and flow) to evaluate the performance of HDC-ICP-MS for the simultaneous determination of dissolved species and nanoparticles of the same element. Special attention was paid to the resolution achieved between dissolved species and nanoparticles (NPs) and their column recovery. The results of the investigation were applied to carry out the metal speciation of different dietary supplements.

Keywords: HDC-ICPMS, nanoparticle, nanomaterial, gold, silver

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TP-62 The potential of single particle ICP-MS for the characterization of metallic nanoparticles in complex clinical and toxicological samples

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Metallic nanoparticles (NPs) have recently attracted great interest in different biomedical applications such as drug delivery systems, therapeutics, biosensors and cancer diagnostics. Nevertheless, the increasing use of these nanomaterials has been accompanied by a growing concern about their safety and potential impacts on human health **[1]**. Therefore, the need of new nanometrological tools enabling to assess the occurrence of NPs in complex matrices such as biological fluids or samples from toxicological studies becomes a new analytical challenge. Among the new approaches for the analysis of metallic NPs, inductively coupled plasma mass spectrometry in single particle mode (SP-ICP-MS) stands up as an interesting alternative. This technique allows a complete characterization of NPs in terms of both particle size and concentration and accomplishes the identification and quantification of many NPs in a short period of time at very low concentrations.

The goal of this work is to study the potential of SP-ICP-MS technique for the detection, identification and quantification of different metallic NPs (gold and platinum nanoparticles, Au-NPs and Pt-NPs, respectively) in complex biological matrices. The experiments were based on the incubation of NPs of different sizes (Au-NPs of 40, 60 and 80 nm and Pt-NPs of 50 and 70 nm) with different biological matrices: a cell culture medium (Dulbecco's Modified Eagle Medium, DMEM), commonly used in *in vitro* toxicological studies, and some clinical samples such as human blood serum or urine. The possible transformations undergone by Au-NPs and Pt-NPs in these complex samples were evaluated by monitoring the particle size and particle concentration. The results of this work reveal that SP-ICP-MS is a promising tool for the characterization of metallic NPs in clinical and toxicological samples which it can be further applicable in clinical trials and toxicological assays to forecast nanotoxicological effects on human health.

Keywords: single particle ICP-MS, gold nanoparticles, platinum nanoparticles, cell culture medium, human serum and urine

Acknowledgements

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TP-63 Different nanoparticles characterization: comparison of different sample introduction strategies using inductively coupled plasma mass spectrometry (ICP-MS)

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The growth of nanoparticles (NPs) application in various fields such as textile industry, cosmetics, food packaging, pesticides, sporting goods, paint, optics, and medical devices have driven the industrial production reaching nowadays $kg.h^{-1}$ **[1]**.

Even though this technology is expected to have major benefits, little is known about their impact on environment and human health.

In order to assess the potential risks that such materials pose, a characterization of nanoparticles (NPs) is needed. NPs characterization includes the determination of mass, size, particle number concentration (PNC), morphology and elemental composition. The ability to detect and quantify NPs in the range of a few nanometers to several hundreds of nanometers still remains a challenge **[2, 3]**. Therefore, comparison and establishing protocols, methods and applications are highly demanded. Inductively coupled plasma mass spectrometry (ICP-MS) is a promising technique which allows fast and sensitive determination of most elements and can be used for analysis of NPs' mass, composition and number concentration **[4]**.

In this work, we use a state of the art sector field ICP-MS, offering high detection efficiency and low instrumental background. However, the inherent sequential detection of the instrument and the fast signal arising from a nanoparticle, limit the detection to only one isotope per NP. Different types of NPs are analyzed including materials that mainly serve for characterization of the instruments (like gold) but also environmentally relevant materials, using higher mass resolving power to separate isotopes of interest from spectral interferences.

As performance study, gold NPs were analyzed using microdroplet generation (MDG) or single particle with conventional nebulization. Moreover, the influence of different operation conditions will be presented, *e.g.* wet and dry plasma condition, nitrogen addition to the carrier gas and the use of a "Jet" interface. The stability of NPs and their change in size and agglomeration state versus time in different media will also be discussed. These data are important in order to ensure that the NP distribution at the point of sampling can be preserved.

Keywords: nanoparticles, SP-ICP-MS, characterization

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TP-64 New calibration approaches for Ag-NPs characterization in complex samples by SP-ICP-MS

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Silver nanoparticles (Ag-NPs) are used in a wide field of applications, such as textiles, household items and food additives. In winemaking processes, Ag-NPs are added as food additives to inhibit the growth of microorganisms and might also be used to replace sulfur oxide (SO_2) as bactericidal agent **[1]**. However, there is a lack of information regarding toxic effects of this type of material on the environment and human health, making imperative the monitoring of NPs in various types of samples **[2]**. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is an emerging technique on nanoparticles (NPs) analysis, providing information as elemental composition, particle number and mass concentrations and size distribution. Although this technique has been strongly developed in recent years, many aspects are still susceptible of improvement, as insufficient multielemental capability, dependency of well-known or reference NPs standards and suitable calibration strategies **[3,4]**. In SP-ICP-MS, an external ionic calibration is required to determine the mass and, consequently, the size of each detected NP. This type of calibration is accomplished by assuming that the transport of ions and NPs through the ICP-MS is approximately the same. However, there are some drawbacks regarding the use of external calibration for NP analysis, such as the mandatory determination of the transport efficiency and sample flux prior to analysis and the high errors susceptibility by the analysis of complex matrices **[5]**.

This work assesses new strategies based on ionic calibration for the characterization of Ag- NPs in complex matrices (*e.g.*, wine samples) by means of SP-ICP-MS. Initially, acidified ionic aqueous standards were used as a base to calculate the size of 75 nm Ag-NPs in 4 different types of wine samples (synthetic, red, white and rose). The diameters were underestimated in all types of samples (34, 47, 40 and 42%, respectively). In order to overcome this drawback, two different strategies were applied: (i) spiking ionic silver in all wine samples, in order to place a standard addition calibration and (ii) using a high temperature total sample consumption system (hTISIS) to mitigate the matrix effects and to investigate the feasibility of using acidic aqueous standards to characterize Ag-NPs in complex matrices. Calibration data, capabilities for the characterization of Ag-NPs and instrumental limits of detection and of quantification were obtained and compared for both methods. This work demonstrates the feasible characterization of Ag-NPs in complex samples using novel calibration strategies for SP-ICP-MS.

Keywords: siver nanoparticles, calibration, SP-ICP-MS

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TP-65 Evaluating TiO_2 nanoparticles in sunscreens by single particle ICP-MS (SP-ICP-MS)

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During the last decade, the production and use of engineered nanomaterials (ENMs) in industrial processes and consumer products has increased dramatically. Because of this, concern has also risen for the effects of nanoparticles on the environment and on human health. These effects need to be carefully evaluated because nanoparticles behave differently than corresponding bulk material.

In consumer's products, titanium dioxide nanoparticles (TiO_2-NPs) are legally permitted in sunscreen formulation up to 25 % concentration **[1]** as UV-filter for the sun's harmful UV rays. Sunscreens contact skin and wash off in water, and TiO_2-NPs can therefore find their way into biological and environmental systems. As a result, there is a need to characterize the number-based size distribution of TiO_2-NPs in sunscreens, as a first step to evaluate their possible impact on human health and the environment, and if the cosmetic product complies with the label claim.

Among the several techniques available to measure nanoparticles, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is an ideal tool for detecting and characterizing element-specific nanoparticles even at very low concentrations. SP-ICP-MS is fast and efficient, and capable to provide information on particle size, size distribution, particles number concentration, and the concentration of an element and of the corresponding dissolved metal ions.

Here we present the results obtained by using SP-ICP-MS to characterize TiO_2-NPs concentration, size and size distribution in commercial sunscreen creams and lotions. For analyses, sunscreens were dispersed in diluted surfactant solution and homogenized by ultra-sonic mixing. Complementary measurements by ICP-OES were carried out to confirm the total content of titanium.

Keywords: nanoparticles, single particle ICP-MS, sunscreens

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TP-66 Development of a novel analytical strategy for the identification and quantification of nanoplastics by ICP- MS

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Nanoplastics are emerging pollutants that affect the marine environment. Million tonnes of plastics produced since last century end up in the ocean, where they suffer continuous degradation and fragmentation into nanoplastics **[1]**. The European Union has acknowledged this problem and the need of better monitoring the occurrence of NPs in the oceans **[2]**. However, up to now, there is little or no monitoring data on the occurrence of this kind of pollution, since its investigation is hampered by the lack of methods able to identify and quantify nano-sized plastics in environmental waters. The objective of this work was to develop an analytical strategy for the quantification of nanoplastics based on the use of metals as tags in order to render the polymer nanoparticles visible for the ICP-MS. Suspensions of two model polystyrene (PS) nanoplastics [one commercial (nominal size; 200 nm), and another synthesized at the lab (size 300-400 nm)] were spiked with different solutions of a metal in its ionic form and fractionated by asymmetrical flow field-flow fractionation (AF4) coupled to ICP-MS. This strategy served two purposes: i) to remove residual free metal ions that may interfere the subsequent quantification and ii) to confirm the presence of the metals adsorbed onto the nanoplastics. The fraction containing the metal-labelled nanoplastics was collected and analysed by ICP-MS in a particle-by-particle mode by adopting the principles of single particle ICP-MS (SP-ICP-MS). The method was optimized by paying special attention to the kind of metal (Ce, Y, Cs and Th were tested) and its chemical form, the concentration of metal spiked, the conditions of the medium and the surface charge of the nanoplastic. From the point of view of the analysis by SP-ICP-MS, critical parameters like dwell time and transport efficiency were studied in detail. The figures of merit of the method will be shown: dynamic linear range, nanoplastic number concentration limit of detection, reproducibility. The developed method can be further applied to model and environmental NPs in order to understand the environmental behaviour of this new class of emerging pollutant in interaction with heavy metals.

Keywords: nanoplastics, SP-ICP-MS

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TP-67 Asymmetrical flow field-flow fractionation hyphenated with ICP-MS for trace level analysis of engineered silver nanoparticles in river water

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Asymmetrical flow field-flow fractionation (AF4) is a powerful tool for the separation of nanomaterials according to their hydrodynamic size. However, significant dilution within the separation channel usually limits its application towards trace level analysis. These limitations can be overcome by taking advantage of two unique features, which this separation technique can offer:
i) Slot outlet **[1]**. Here, the channel outlet flow is split into two separate flows. Since the sample is usually located close to the semi-permeable accumulation wall in the lower 5-10% of the channel, the upper sample-free void volume can be removed thereby reducing sample dilution; ii) High volume injection **[2]**. In AF4, a focusing or relaxation step is necessary prior to elution, where sample components arrange in different heights of the separation channel according to their different diffusion coefficients counteracting with an external force field. This is realized by a second flow, the so called cross flow, which acts perpendicular to the channel flow and pushes the sample components towards the accumulation wall. During sample introduction, a focus flow, which counteracts the sample injection flow, hereby enables virtually unlimited sample introduction and thus sample enrichment directly on the separation channel and defines the starting line of the fractionation. iii) Hyphenation with a high-sensitivity detector ICP-MS **[3]**. ICP-MS is particularly powerful, when it comes to the chemical identification and quantification of metallic and metal oxidic sample components such as *e.g.* silver nanoparticles (Ag-NPs). Hence, its hyphenation with AF4 (AF4-ICP-MS) enables the collection of data on elemental composition over the size distributions even at trace concentration levels.

In this presentation, we demonstrate the applicability of AF4-ICP-MS for the quantification of Ag-NP spiked in Rhine water at trace level concentrations. Using an injection volume of 8 mL along with a 60% Slot-outlet, Ag-NP down to 14 ng.L^{-1} (LOQ) could be quantified.

Keywords: asymmetrical flow field, flow fractionation, silver nanoparticles, ICP-MS, trace level analysis, hydrodynamic size

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TP-68 Extracting nanoparticles: how is it done in SP- ICP-MS with microsecond time resolution, when continuous background is present?

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In SP-ICP-MS, nanoparticles (NPs) are detected as spikes above a steady background (BG). A continuous data acquisition system with up to 5 s time resolution for SP-ICP-MS **[1]** makes it possible to obtain ion clouds profiles of NPs. This fast detection significantly decreases the BG, since it is distributed over several dwell times, and *e.g.* 50,000 cps become 0.25 counts in 5 s. As only positive integer numbers can be the detector output, 0.25 counts in 5 s mean that the chance to detect one count in 5 s is 25%. This significant decrease in continuous BG makes it much easier to extract NPs and decrease their size detection limit. However, how can one be sure that only NPs and not the BG are extracted?

A mathematical approach to extract NPs from the BG **[1]** and statistical principals to ensure quantitative NPs determination will be introduced. On an example of different BG, it will be shown how extraction conditions affect the obtained NPs size distributions. The definitions of detection limits will be revisited and explained for ion clouds represented by profiles and not only single intensity values.

Keywords: SP-ICP-MS, microsecond time resolution, data processing, dissolved, limit of detection

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TP-69 Heteroatom incorporation during MFI crystallization as measured by single particle inductively coupled plasma mass spectrometry

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In this study, we used, for the first time, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) to determine the presence of heteroatoms in MFI nanoparticle solutions. This new SP-ICP-MS method gives the unique ability to monitor heteroatom incorporation into zeolite particles as a function of reaction time. Multiple samples were taken over various time points of the zeolite synthesis and were analyzed by this technique. The results showed different uptake into the MFI-zeolite crystal for the various heteroatoms of interest (Al, Fe, W of interest). In this presentation, we report nanoparticle concentrations and particle size distributions for all zeolite samples. This study demonstrates the applicability of SP-ICP-MS to characterize heteroatoms and compares the results with other characterization techniques.

Keywords: SP-ICPMS, zeolite

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TP-70 Investigating the impact of nano-pesticides on plants, soil and waste water sludge using SP-ICP-MS

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Engineered nanomaterials (ENMs) used in various applications can improve the performance of many consumer and industrial products, for example in food and agriculture, personal care products, paints and coatings, water treatment and medicine. The production volume of ENMs has increased rapidly over the past decades due to new applications. The growing use of ENMs has raised concerns about their potential implications to the environment and human health. Over the past decade, increasingly more information has become available regarding the potential environmental implications of ENMs, including the estimates of the release of ENMs from products; the fate-and-transport of ENMs between different environmental compartments after release; the long-term behavior of ENMs in environment compartments and organisms; the toxicity of different ENMs; the sensitivity of different species to ENMs; potential human exposure to ENMs and their behavior in the human body. However, a major challenge has been the development of analytical techniques to detect their presence and determine their concentration in water, waste water and soils. In this presentation, the use of single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) as an emerging analytical technique for this novel class of materials will be presented.

Keywords: engineered nanomaterials, SP-ICP-MS

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TP-71 Analysis of chromium immobilization on zero- valent iron nanoparticles by ICP-OES

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Nanomaterials have attracted the greatest interest as a fast growing class of materials for very different kind of applications considering their various properties, such as their increased reactivity at lower level **[1,2]**. Practical functionality of zero-valent iron nanoparticles (nZVI) is broadly customized in procedures such as analytical preconcentration and extraction. It is due to their chemical stability, large surface area, durability, corrosion resistance and cost effectiveness. Many recent studies have put in focus reductive immobilization of potentially toxic metal species on iron nanoparticles. For the determination of removal efficiency, scanning emission microscopy or X-ray diffraction (XRD) are often used. However, there is a lack of studies concerning the changes of solution, especially aqueous solution **[3]**.

In this work, the ICP-OES method for quantitative analysis of chromium (VI) removal from water by nanoscale iron was applied. Zero-valent iron nanoparticles (nZVI) were freshly prepared by reduction of ferric iron with sodium borohydride. The morphology of prepared particles were characterized by XRD and SEM analyses. The extraction capabilities of synthesized particles were tested on model aqueous solutions containing hexavalent chromium species. The initial concentration range of Cr (VI) in water solutions was adjusted from 0.1-100 ppm. Reductive immobilization of hexavalent chromium on nZVI was examined in two sets of experiments. The first one was performed with bare nanoparticles and the second one with modification of surface by addition of 1,5-diphenylcarbazide that is common reagent in chromium speciation. Separation of particles from solution was achieved using solid phase extraction (SPE). The chromium content was determined in filtrate solution and in separated particles that were dissolved before ICP-OES analysis. Measurement was performed on several chromium lines of different sensitivity. The removal of chromium was maximally efficient (95%) at concentration range up to 2 ppm. The efficiency of removal decreased in upper range (43-21%). By comparison of two sets of experiments, it was observed that slightly better removal efficiency is showed after functionalization of nZVI particles with 1,5-diphenylcarbazide and it was more pronounced in lower concentration range.

ICP-OES determination has confirmed the immobilization of chromium (VI) on nZVI particles. Moreover, it was helpful in estimation of magnitude of adsorption that occur on nanoparticles surface in aqueous solutions.

Keywords: chromium (VI), ICP-OES, iron nanoparticles

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TP-72 Use of a mini-channel in AF4-ICP-MS for detection and characterization of titanium dioxide nanoparticles in consumer products

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One of the most representative cases of the current trend in the field of nanotechnology is titanium dioxide (TiO_2), mainly due to the increase in its use in a large variety of consumer products. Because of its properties at nanometric scale (1-100 nm), such as photocatalysis, TiO_2 nanoparticles can be found in sunscreens, cosmetics, food packaging and surface coating. These nanoparticles are also used in environmental remediation, as food additive or as whitening pigment. Due to the disparity of products and possible scenarios where these nanomaterials can be present, it is evident the need for the development of new methodologies which can contribute to obtain more information in addition to that provided by more conventional techniques, namely electron microscopies or light scattering-based techniques.

This work is focused on the use of asymmetrical flow field flow fractionation (AF4) coupled to UV-Vis spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS), for the detection and characterization of dioxide titanium nanoparticles (TiO_2-NPs) in complex samples. In this study, the use of a channel of reduced length is proposed, instead of a channel of conventional dimensions, in order to safe analysis time and reduce cost, without sacrificing resolution or recoveries. Besides, resolution can be improved keeping the same crossflow and channel flow conditions.

With this purpose, the variables that determine the separation process in AF4 have been analysed and optimized, in terms of resolution and recoveries. The characterization is based on the comparison of several strategies for size calibration, including the use of different size standard suspensions (such as polystyrene or SiO_2) commonly used in AF4. Finally, the methodology will be applied to the detection and characterization of TiO_2-NPs in complex samples from consumer products such as metallic food painting, which contains TiO_2 as an additive (E171).

Keywords: AF4-ICP-MS, nanoparticle, nanomaterial, titanium dioxide

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TP-73 AF4-ICP-MS as a powerful tool for the study of platinum nanoparticles in water samples

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The use of engineered nanomaterials has increased rapidly in different fields over the last decades. Among these nanomaterials, metallic nanoparticles and specifically platinum nanoparticles (Pt-NPs) present exceptional catalytic reactivity which makes their use convenient for catalytic converters in vehicles **[1]**. Nevertheless, mechanical abrasion and chemical reactions at the catalyst surface may cause Pt-NPs emission through exhaust gasses of vehicles **[2]**. Those emissions could lead to dispersion and accumulation of Pt-NPs all over environmental compartments, requiring setting the potential associated risks. This is indeed a challenging task and the development of novel and powerful analytical techniques able to provide reliable information is necessary for fully understand their fate and behaviour **[3]**.

For this purpose, new analytical methods such as the coupling of hydrodynamic separation techniques with elemental specific detectors must be developed. One of the most promising combination is asymmetric flow field flow fractionation coupled to inductively coupled plasma mass spectrometry (AF4-ICP-MS). AF4 has some advantages over other separation techniques, such as minimal sample preparation, high separative power at the required size ranges and its wide application range **[4]**. ICP-MS as a detector is also advantageous due to its high sensitivity, selectivity and multielement capability. This AF4-ICP-MS hyphenated system can give simultaneous information about particle size range, concentration and composition, but there are nearly not applications for Pt-NPs in environmental samples.

In this work, a sensitive and selective analytical method for the determination of Pt-NPs in water samples by AF4-ICP-MS has been developed. Optimal separation conditions, such as carrier flow and composition, injection time or cross flow, were found leading to adequate resolution and quantitative recoveries. Also, the developed method has been applied to study Pt-NPs behaviour in synthetic water samples. Moreover, the effect of NPs size and humic acid concentration on Pt-NPs's stability was tested over time.

Keywords: platinum nanoparticles, AF4, hyphenated techniques, water

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TP-74 Simultaneous measurement of multiple isotopes and elements in nanoparticles using a multi-collector ICP-MS with microsecond speed electronics and wide range Daly ion counters

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Single particle ICP-MS (SP-ICP-MS) is becoming a well established technique for the measurement of low concentrations of metal and metalloid nanoparticles **[1]**. The requirement for high speed analysis where the instrument measurement time (dwell time) is substantially shorter than the duration of the signal from a nanoparticle is also now well established as the best way to achieve low detection limits and measure more accurate particle number concentrations **[2]**. Most SP-ICP-MS work to date has focussed on the measurement of a single isotope which is satisfactory for many applications where combination with sample introduction techniques such as field flow fractionation can provide the additional information required to help determine overall particle characteristics. Some applications are better served though by being able to simultaneously measure multiple isotopes or elements, for example investigating core/shell particles where the distribution of core versus shell needs to be known compared to size. Attempts to address this have been made by using fast peak jumping on quadrupole ICP-MS which has difficulties with reduced sensitivity and errors created by the sequential measurements only allowing 1 or 2 measurements per particle with significant signal skew. Data has also been reported using a time of flight ICP-MS but with significantly reduced sensitivity meaning smaller particles can not be measured with reasonable precision **[3]**.

This work will describe the use of new ion counting electronics fitted to a Nu Plasma II multi-collector ICP-MS with Daly detectors. Dwell times of tens of microseconds with continuous, uninterrupted data collection on several channels will be presented. Data will be shown for isotope and element ratios for a range of core shell particles demonstrating the benefits of sensitivity from the magnetic sector ICP-MS for smaller particles. The work will also show the extended dynamic range possible with the Daly ion counters which have proven to be linear to count-rates equivalent to 40 mcps.

This work will show data to investigate that hypothesis that it may be possible to determine the construction of a particle from the signal profiles where the signal from the core element trails the signal from the shell and suggest some mechanisms for the findings from the data.

Keywords: nanoparticles, multicollector, single particle ICP-MS

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TP-75 Calculation considerations for characterizing silver nanoparticles with different properties in environmental samples by single particle inductively coupled plasma mass spectrometry

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In the last years, the production of silver nanoparticles (Ag-NPs) has rapidly increased, enhancing their release in the environment and consequently generating a concern for the adverse effects that they can cause to organisms. Nanoparticle properties such as particle size or surface chemistry may be related to toxicity. Therefore, nanoparticle characterisation is important to understand the toxicity that can exert these emerging compounds to the environment. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) technique has demonstrated its ability to detect and characterize metal-containing nanoparticles in aqueous matrices at relevant environmental concentrations. However, it is still challenging to obtain accurate and consistent particle sizes, size distributions and particle number concentrations due to none existence of validated calculation methods. Furthermore, the use of these methods is often limited by the scarcity of certified reference materials for calculating nebulization efficiency (ηeb) that is the parameter needed for nanoparticle characteristics measurement. ηeb can be calculated by three different calculation methods, being particle frequency method and particle size method the ones that are usually employed **[1,2]**.

In the present contribution, the potential of particle frequency method and particle size method was tested for calculating ηeb using commercial well characterized Ag-NPs standards (100 nm citrate-Ag-NPs; 75 nm and 100 nm polyvinylpyrrolidone-Ag-NPs; 100 nm polyethylene glycol- Ag-NPs) instead of certified reference materials. Results showed some differences between ηeb based on particle frequency method and particle size method. Although, particle sizes determined with ηeb size-based calculation method were closer to manufacturer's value than the ones obtained by ηeb frequency-based calculation method, no significant statistical differences were observed between particle diameters calculated with ηeb frequency-based measures and manufacturer's value.

Another challenge in environmental sample analysis by SP-ICP-MS is the discrimination of ionic silver (Ag(I)) and/or background signal from Ag-NPs signal, that is crucial to accurately determine some nanoparticle properties. In this study, different algorithms, proposed in the bibliography, were tested, analysing a standard solution of 100 nm citrate-Ag-NPs and a mixture of 75 nm polyvinylpyrrolidone-Ag-NPs and Ag(I). Results indicated that the algorithm which better avoid the appearance of false positives (Ag(I) or background signal counted as Ag-NPs signals) was the one based on Laborda *et al.* **[3]** in comparison with the other studied algorithms.

Finally, the selected methods were used for Ag-NPs characterisation in a soil aqueous leachate containing a mixture of Ag-NPs and Ag(I).

Keywords: silver nanoparticles, single particle inductively coupled plasma mass spectrometry, particle frequency method, particle size method

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TP-76 Characterization of silver species released from clays coated with silver nanoparticles in *in vitro* gastrointestinal digestion using AF4-ICP-MS

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In the last decades, several types of additives have been proposed in animal production as alternatives to the use of antibiotics as growth promoters, banned by the European Union in 2006. Within these, group silver nanoparticles are a promising alternative, since they have a higher antimicrobial effect and also a lower absorption through the intestinal mucosa. Clays (kaolinite and sepiolite) coated with silver nanoparticles included in the diet have been proposed for administration of silver to animals.

The characterization of the silver species released from these materials was carried out along the different stages of *in vitro* gastrointestinal digestions in order to study the possible transformations of silver in these conditions and to understand the effects of the use of these materials on the digestive microbial ecosystem. This characterization was made by asymmetric flow field-flow fractionation (AF4) coupled to an inductively coupled plasma mass spectrometer (ICP- MS) as an element detector. This technique allows the detection and the size characterization of the potential released silver nanoparticles, silver associated with kaolinite or sepiolite microparticles, as well as other macromolecular species present in the complex media that can be associated with silver (I). The ionic silver fraction or associate to low molecular weight species, which is not possible characterise by AF4, was isolate by ultrafiltration with membranes of small pore size (3 kDa equivalent to ca. 2 nm) and it was quantified by ICP-MS. The study of the behaviour of materials in simple leaching media (such as ultrapure water or HCl 0.01mol.L^{-1}) allowed to establish the importance of the carrier composition used for AF4 separation.

Keywords: AF4-ICPMS, nanoparticle, nanomaterial, *in vitro* digestion

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TP-77 Detection of nanoparticles released from metallic food additives by single particle ICP-MS

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The use and occurrence of nanoparticles in food products is raising serious concerns about their potential risks. In this regard, the European Food Safety Authority (EFSA) recently published a guidance on human and animal health aspects of the risk assessment of nanoscience and nanotechnology applications in the food and feed chain **[1]**. One of the main conclusions was that the need for standardized methods for analytical characterization and risk assessment still exists.

The current list of food additives approved by EFSA includes three metals: aluminum (E173), gold (E175) and silver (E174). The three of them are authorized to be used to color the external coating of confectionery, although the information available about these additives is still insufficient to assess their safety.

In this work, the transformations of metallic silver and aluminum present in foods were studied along the digestive process. Foods containing the additives were subjected to *in vitro* gastrointestinal digestion. Next, digestates from the oral, gastric and intestinal steps were analyzed by ICP-MS to quantify the amount of the metals released, as well as to identify their physico- chemical forms. Although a significant proportion of the metals was released as ionic species, single particle ICP-MS proved to be effective for the rapid detection of nanoparticulate forms of the metals even in the presence of their dissolved counterparts.

Keywords: single particle ICP-MS, nanoparticle, nanomaterial, food additive, in, vitro digestion

Acknowledgements

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TP-78 New algorithms for enhancing particle detection in SP-ICP-MS

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The particle-related spikes caused by small nanoparticles in SP-ICP-MS usually overlap with the random noise of the dissolved signal, even when relatively short dwell times are used. Creating algorithms for distinguishing the smallest particle events possible in noisy data is therefore necessary for the development of SP-ICP-MS.

Our current work focuses on outlier detection-based algorithms that, besides from identifying particles based on their intensity, also use deviation from normal distribution of the ion bursts as a criterion. When using relatively short dwell times, more than one data point per particle event is detected and the shape of these events can thus be used as a criterion to identify particles, based on the fact that time-dependent particle events tend to be Gaussian in shape with the half- peak width falling into a relative narrow range, whereas dissolved signal noise and disturbances have more diverse appearances. The accuracy of this shape-based detection is evaluated by detecting Au nanoparticles of increasing size with varying concentrations of spiked dissolved analyte.

A second algorithm adapts the deconvolution-based algorithm that fits Polya-Gaussian distributions to the dissolved signal, an algorithm that was developed mathematically to also describe dissolved signals obtained at relatively short dwell times. The randomly formed peaks were integrated similarly to signals of particle containing samples. The probability of randomly forming peaks within the peak integration window is calculated. The particle events in excess of this number can be removed and the calculations are repeated with the reduced dataset as long as new particles are found.

The algorithms will be implemented into freely available software (NanoCount) to make them available for a wide audience.

Keywords: nanoparticle algorithm, single particle, peak detection, data ananlysis software, ICP-MS, nanomaterial

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TP-79 Nanoparticle analysis in semiconductor grade chemical reagents

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To meet evolving requirements for higher integrated circuit (IC) performance and improved semiconductor device yield, contamination must be controlled in the wafer substrate and on the surface of the device during fabrication. Given the nanometer scale of device features, currently 10 nm line widths, there is a critical need to monitor metallic nanoparticles (NPs) as well as dissolved metals in bulk chemicals and wafer processing and cleaning baths. Also, multi-elemental analysis of NPs is necessary to fully investigate the cause of particle contamination.

ICP-MS is a well-established and widely used technique for measuring high purity semiconductor grade reagents because of its high sensitivity. More recently, there has also been growing interest in characterizing NPs in various semiconductor samples using the single particle ICP-MS (SP-ICP-MS) technique. SP-ICP-MS is used to measure the target element signals generated from individual NPs in the solution being analyzed.

In this study, we will present results of metal NP analysis of semiconductor grade reagents such as TMAH. The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) is suited to the application because of its superior sensitivity and interference removal capability. Also, Agilent has developed a rapid multi-element nanoparticle analysis function for ICP-MS MassHunter software. The multi-element mode software can collect data sequentially for up to 16 elements in a single sample analysis, using optimum conditions for the measurement of each individual element. This function saves time and reduces the risk of sample contamination compared to conventional SP- ICP-MS analysis, as the multi-element analysis requires only one visit to the sample vial.

Multi-element NPs, including SiO_2, Fe_3O_4, and Al_2O_3,were spiked into high purity chemical reagents. Details of the multi-element NP method and performance data will be presented.

Keywords: nanoparticles, single particle ICP-MS, SP-ICPMS, semiconductor

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TP-80 Determination of substrate-assisted laser desorption ICP-MS transport efficiency of gold nanoparticles

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Substrate-assisted laser desorption inductively coupled plasma mass spectrometry (SALD ICP-MS) is a method for fast determination of metals from dried droplets of sub-microliter sample volumes applied onto a polymer substrate, such as polyethylene terephthalate-glycol (PETG) **[1]**. Besides using SALD ICP-MS for determination of metals in dissolved forms, it can also be used for analysis of metal nanoparticles in single particle (SP) mode **[2]**. An important parameter of SALD SP-ICP-MS is transport efficiency; transport efficiency of 56 nm gold nanoparticles (Au-NPs) was estimated to be around 60%. This contribution describes the development of a more direct method for determination of SALD transport efficiency using scanning electron microscopy (SEM).

A thin chromium layer was deposited on PETG plates using a sputter coater (Q150T ES, Quorum Technologies, UK) in order to make the surface of PETG plates conductive. The stock suspension of 80 nm Au-NPs (1E+10 NPs/mL, BBI solutions, UK) was diluted 70 times and volume of 3.5 nL was deposited using a piezoelectric dispenser (MJ–ABP–01–50–DLC, MicroFab Technologies, USA) on polyethylene terephthalate glycol (PETG) plate and dried yielding about 500 Au-NPs in a dried droplet. The diameter of the dried droplet was 60 m. In order to determine the exact number of Au-NPs in a droplet, the stains were imaged using SEM (Helios 4 CX DualBeamTM, Thermo Fisher Scientific, USA). Only 106 x 106 m square area containing the stain was left for further analysis, the surrounding chromium layer with occasionally present Au-NPs was removed with Ga ion beam (Tomahawk Ion column, 30 kV, 65 nA). The squares with dried droplets were desorbed using a raster scan with 213 nm laser ablation system (UP213, New Wave Research, USA). Signal at *m/z* 197 was acquired by an ICP quadrupole mass spectrometer (7500ce ICP-MS, Agilent, USA) with integration time 10 ms. The overall transport efficiency of 45 % was determined from numbers of Au-NPs determined by SALD SP-ICP-MS and SEM. Ways to enhance transport efficiency will be discussed.

Keywords: SALD ICP-MS, nanoparticle, nanomaterial, transport efficiency, substrate–assisted laser desorption

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TP-81 Analysis of nanoparticles in organic solvents using single particle ICP-MS with multi-spray CGrid nebulizer

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is an emerging analytical technique that can determine the compositions, ionic and particulate concentrations, and the sizes and size distributions of inorganic nanoparticles (NPs). One of the major technical challenges is the matrix effect. For example, mismatching of matrices in sample suspension and calibration solution such as ionic solution or standard particle dispersion causes a quantitative errors of particle diameter up to 90% **[1]**. Matrix matching are the best way to compensate the matrix effect, but it is difficult to prepare both sample suspensions and ionic solution (or particle standard suspension) with the same matrices. Especially for dispersing nanoparticles, while some organic solvents are frequently used for well dispersing, there are concerns about instability of ionic standard solution for calibration if the matrix solvent was matched. In addition, some organic solvent and water solutions hardly achieve a homogeneous mixing. For overcoming the issue to realize stable matrix matching, we developed a new multi-spray type concentric grid nebulizer adapted for microflow (microflow m-CGrid). It has a unique structure, one nozzle with a grid screen and two independent liquid flow lines set inside the nozzle. The liquids are well-mixed in a small space just before the grid screen, because the grid acts as a dumper. The mixture of the liquids breaks-up into small droplets by passing through the grid, resulting in simultaneously and efficiently nebulizing two liquids without pre-mixing before introducing into the nebulizer.We applied microflow m-CGrid with an on-axis cylinder chamber for the evaluation of the size and number concentration of nanoparticle suspended in some polar and non-polar organic solvents using SP-ICP-MS, where two sets of an automatic switching valve and a syringe pump were used for individual sample and standard introductions. We will present the results of validation of the system by analyzing commercially available nanoparticle standard materials.

Keywords: nanoparticles, matrix matching, sample introduction, nebulizer, organic solvents

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TP-82 In vitro gold nanoparticles uptake into tumour cells : an analysis by SP-ICP-MS

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Nanoparticles are increasingly used in cancer diagnosis and therapy; in particular, gold nanoparticles are studied as promising contrast agents and as radiosensitizer in X-ray. But improving the dose received by tumour cells requires a control in terms of qualification and quantitation of the gold nanoparticles uptake into cells. In our study, the uptake of pegylated 32nm gold particles was investigated *in vitro* in two types of human cancer lines. Particle number concentrations and gold mass fractions were analyzed by single particle ICP-MS after alkaline digestion. In addition, the uncertainties on the gold mass fractions by single particle ICP-MS and by conventional ICP-MS were calculated. After optimization of the sample digestion procedure, we show that the analysis with SP-ICP-MS were able to achieve total gold recovery for all samples. These first results will be useful to better understand the uptake route of particles in tumour cells for application in future cancer treatment. Overall, these experiments confirm the efficiency of SP-ICP- MS for nanoparticles analysis in biological samples and for *in vitro* studies, but stress the need of careful sample preparation and data treatment for SP-ICP-MS analysis.

Keywords: SP-ICP-MS, gold nanoparticles, tumour cells

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TP-83 Analysis of titanium dioxide nanoparticles in biological fluids using single particle ICP-MS

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Titanium dioxide nanoparticles (TiO_2-NPs) are widely used in sunscreens, toothpastes or some technologies for their UV filtering properties, whitening agent or for photocatalytic purposes. Because of this important use, there are concerns about the potential health risk. Indeed, due to their small size, NPs can cross biological barriers, be distributed in the human body through blood and thus be accumulated in various organs or be transformed/excreted.

Therefore, it is essential to be able to measure them, determine their physico-chemical properties in biological fluids such as urine and blood.The metrology of NP is currently insufficient and clearly requires the development of innovative technologies to determine the main characteristics (size and size distribution, agglomeration and aggregation state, mass and number concentration, shape) and thus to assess human exposure.

In recent years, the single particle ICP-MS technique is gaining attention. It provides simultaneous information on the presence of dissolved ions and NPs, the determination of the NP size distribution, the dissolved metal mass concentration and the NP number concentration. This project is based on the development of a method by SP-ICP-MS to detect and characterize TiO_2-NP in biological fluids.

The major challenge was the preparation of a stable suspension of TiO_2-NP. Indeed, they have strong tendency to agglomerate or aggregate which causes an overestimation of the size and an underestimation of the concentration. Various parameters have been studied such as suspending media and sonication mode in order to obtain an optimized sample preparation stable overtime. Dynamic light scattering was then used to verify the suspension stability. Following these optimization steps in aqueous matrices, the method has been tested on biological fluids which consists in adding a known concentration of TiO_2-NP in blood and urine. It allows us to adapt the method to the needs and then to assess human exposure.

The research project should lead to the development and validation of an innovative analytical method which will serve as a reference base for NP metrology in biological media. Its application in the assessment of human exposure to NPs could represent an important advance in the overall understanding of innocuity or toxicity of NPs.

Keywords: single particle ICP-MS, TiO_2-NP, biological fluids

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TP-84 Overcoming spectral overlap in the characterization of iron nanoparticles by means of single-particle ICP-mass spectrometry (SP-ICP-MS): chemical versus physical resolution

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In comparison to larger scale materials with the same chemical composition, nanomaterials (NMs) have different physical, chemical and/or biological properties. As a result, the use of NMs is growing very rapidly and their characterization is one of the topics of high interest within the scientific community. VITO (Flemish Institute for Technological Research) synthesizes, characterizes and functionalizes various NP types. Iron nanoparticles (FeNPs), which are of special interest owing to their magnetic properties in *e.g.*, environmental and/or biomedical applications, is one of the NP types VITO pays attention to.[1, 2]

Different analytical techniques have been developed for the characterization of NPs, but inductively coupled plasma-mass spectrometry (ICP-MS) operated in single-particle (SP) mode is one of the fastest growing approaches nowadays. SP-ICP-MS provides different types of relevant information, such as chemical composition, size distribution, particle number density and mass concentration.[3, 4] However, the use of SP-ICP-MS becomes less straightforward for NPs affected by spectral interferences, such as the ubiquitous Ar^+ polyatomic ions with the same nominal mass- to-charge (m/z) ratio as the most abundant Fe isotope. Over the years, different ICP-MS approaches have been developed to address spectral overlap in ICP-MS, the use of collision/reaction cell (CRC) technology in quadrupole-based ICP-MS (ICP-QMS) and of high mass resolution in sector-field ICP-MS (HR-SF-ICP-MS) being the most important.[5, 6] So far, ICP-CRC-QMS instrumentation has been widely applied for the characterization of NPs, although HR-SF-ICP-MS instruments have also shown potential in this context.[7] In addition, the development and/or further refinement of such instrument types (*e.g.*, faster scanning processes, lower dwell times, pseudo-high mass resolution and user-friendly software) might potentially enhance the use of sector-field technology for NP characterization in the near future.[8-11]

In this work, commercially available and in-house synthetized FeNPs have been characterized by means of these two different ICP-MS technologies and the figures-of-merit attainable using both chemical (CRC technology) and physical (pseudo-medium) resolution have been assessed and will be reported on into detail.

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Keywords: iron nanoparticles, SP ICP MS

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TP-85 Comparison of SP-ICP-MS and SMPS: Different measurement principles for the determination of the size of nanomaterials

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Metallic nanoparticles (NP) are applied in numerous industrial and consumer products where they play an increasingly important role. A striking specificity is their high volume to surface area ratio, which is due to their nano size dimension. To describe the physicochemical properties of NP in an exact manner, the precise and repeatable determination of its size, number and number concentration becomes crucial.

However, the characterization of different metallic and metal oxide NP according to these key parameters is still in its infancy. This is especially true for airborne particles, where the size and number determination as well as the chemical analysis are performed by using the very same sample. For determination of these numbers, a variety of methods can be utilized. For instance, measurement techniques such as inductively-coupled plasma mass spectrometry (ICP-MS) focusing on single quadrupole instruments and scanning mobility particle sizing techniques (SMPS) are widely used. These techniques exhibit distinct advantages and limitations. A comprehensive description of possible interferences affecting the respective techniques would be helpful to enable a cross-evaluation of particle property determination.

SMPS is best suited for an unspecific size determination of primary particles in samples with high background. Bimodal particle distribution is possible. In contrast, single particle (sp-) ICP-MS allows an element-specific differentiation of primary particles and a precise characterization of individual particle size populations including their respective particle number concentration. The working range of the SMPS is highly adapted to high particle loads, but the particle related signal must be clearly distinguishable from the background. Conversely, sp-ICP-MS has a size limitation due to the ionic background signals.

To ensure the highest compliance of the measurement techniques applied, the same nebulizers (conical and cyclone) were used in both systems. Preliminary results confirm the influence of the sample introduction systems. The cyclone chamber removes bigger particle agglomerates because of the geometry of the chamber. A more realistic size distribution is obtained with a conical chamber. This characteristic is especially important for NP with a tendency for agglomeration, sedimentation and dissolution.

Not only the detections system but also the sample inlet system has to be carefully selected for the analytical task at hand. In general SMPS is useful for complex and highly concentrated samples and SP-ICP-MS is better suited for well-defined samples in the low concentration range.

Keywords: nanomaterials, single particle ICP/MS, nebulizer

TP-86 Nanoparticles biodistribution studies: Optimization of lung digestion protocols for TiO_2 NPs analyses by SP-ICP-MS

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The biodistribution of inhaled nanoparticles (NPs) into the lungs is an important feature to better understand their toxicity.

Inductively coupled plasma mass spectrometry (ICP-MS) is at that time the most used tool to quantify (oxide) metallic NPs in organs or tissues. It implies a sample mineralization and therefore a dosage of the metal in ionic form. In the nanotoxicology field, it is important to distinguish the substance form (particulate/ionic) as it could modulate the toxicity. Inductively Coupled Plasma Mass Spectrometry used in a single particle mode (SP-ICP-MS) appears to be the technique of choice to measure in a single analysis the nanoparticle number concentration, the size distribution and the ionic concentration of a sample. Many studies exist on quantifying gold or silver NPs using sp-ICP-MS in aqueous suspension but few on titanium oxide NPs in biological matrices.

To perform an ICP-MS analysis in single particle mode, a digestion of the organ is required. It must involve a protocol strong enough to remove all the organic matter, but gentle enough to avoid nanoparticle grain-sized modification. In this study, we first compared the efficiency of two digestion methods, an enzymatic digestion and an alkaline digestion. Thus, a rat lung was spiked (miming an intratracheal instillation) with a known quantity of TiO_2 NPs (NM100 from JRC) in suspension. This spiked level was around 1 g/L. It is not related to a real exposition but was chosen only to evaluate the performance of the two protocols. Then, the spiked organ was homogenized using a freezer mill and afterwards digested with TMAH (Tetramethylammonium hydroxide) for the alkaline digestion, and proteinase K for the enzymatic digestion. Finally, analyses were done by two approaches:

- a total quantification (acid mineralization and ICP-OES analysis) of Ti to evaluate the yield of recovery.
- a SP-ICP-MS analysis to assess if the concentrations measured after an enzymatic or alkaline digestion are similar to the classic ICP-MS concentration measurement.

Enzymatic digestions show the best yields with a good reproducibility.

Single particle-ICP-MS analyses are still processing and seem to agree with total concentration values.

Keywords: nanoparticles, single particle, ICPMS, enzymatic digestions, alkaline digestions, biodistribution, inhalation

TP-87 The role of single particle ICP-MS with microsecond time resolution in a multi-technique approach for unveiling the biological fate of ingested nanoparticles

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In the food sector, applications of nanotechnologies to agricultural production, food processing, and food contact materials are rapidly developing. Nanotechnology applications in the food sector may bring benefits; on the other hand, potential risks have to be assessed and excluded. Relevant information for performing an appropriate nano-specific risk assessment is also required for a number of currently used food additives and nutrient sources in particulate form, which are not nanotechnology products but present a substantial fraction of nano-sized particles.

The recent EFSA Guidance for nano-specific risk assessment set out a framework for step- wise hazard identification and characterisation **[1]**. The first step investigates whether the nanomaterial undergoes a quick degradation (e.g. dissolution) under conditions representative of the gastrointestinal tract, thus losing the nanoparticulate nature. Nanomaterials that quickly dissolve/degrade in the gastrointestinal tract do not give rise to nano-specific concerns and standard risk assessment can be followed. Only if nanoparticles persist as such after gastrointestinal digestion they may be absorbed in the gut. In this case, it is necessary to investigate their stability of under lysosomal conditions to assess the potential for intracellularaccumulation.

Within the NANOPERSIST project, the time-dependent transformations of nanoparticles under conditions representative of the gastrointestinal tract and lysosomes have been studied by robust in vitro methods with standardised protocols complying with the guidance [1]. A state- of- the-art multi-technique approach (transmission electron microscopy, single particle ICP-MS, AF4- UV-MALS-ICP-MS/MS, centrifugal liquid sedimentation, dynamic light scattering) has been used for the physicochemical characterization of the particles in pristine conditions, after ingestion in fed and fasted conditions, and after lysosomal processing. Ten different materials belonging to four chemical classes (synthetic amorphous silica, titanium dioxide, iron oxides/hydroxides, and zinc oxide) were studied. TEM was essential to study particle morphology and primary size. DLS and CLS gave an insight about the agglomeration behaviour of the pristine material at different pH conditions. However, only spICP-MS with the use of µs dwell times combined with ion–molecule chemistry for resolution of spectral interferences enabled to obtain quantitative data on the mass concentration and number-based distributions in biological simulated fluids for most material types.

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PLW-1 Contributions to automated element imaging by laser ablation inductively coupled plasma mass spectrometry

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Direct solid micro analysis using laser ablation in combination with inductively coupled plasma mass spectrometry (LA-ICP-MS) has become a standard technique for geologists and current developments focus on geological and medical applications, mainly imaging of thin-sections or tissues. Recent improvements in time-of-flight (TOF) mass analyzers contributed to a more flexible element imaging. Therefore, a tight software control of sample position, laser pulse sequence, and ICP-MS data acquisition enable superior performance in terms of sensitivity, limits of detection, and image contrast over more line scans. Such a program has been developed in our group and the software implementation includes a communication interfaces to an ArF excimer laser ablation system (193 nm, GeoLas C, Lambda Physik, Goettingen, Germany) triggered by a separate microcontroller (Arduino Uno). The firmware for the microcontroller was also developed in-house. Moreover, positioning controls were implemented for the translation stage (SLC-24 series and MCS-3 controller, SmarAct GmbH, Oldenburg, Germany) used in the setup. New communication interfaces were added due to the modular design of the software allowing inclusion of different hardware setups. As programming language, Python 3 was chosen to profit from its large library support as well as its popularity in the scientific community. The conjunction of this laser ablation system and an ICP-TOF-MS (icpTOF, Tofwerk, Thun, Switzerland), allows for precise laser pulse or pulse sequence triggering of TOF data acquisition in order to store spectral information sample position specific and thereby simplify data processing and analysis.

The ablation pattern and laser ablation mode can be customary fitted to the sample and analytical aims: more conventional high spatial resolution fast imaging with edge-to-edge laser spots for compositional overview or hole drilling, where multiple laser shots are applied to the same sample position, for improved sensitivity and contrast. Furthermore, custom ablation area masks can be customarily fitted to a sample's specific structures.

We demonstrate the capabilities of this approach with examples from current geological research: the analysis of multiple fault rock samples from a nuclear waste repository and show some examples from an ilvalite rosette.

Furthermore, the 100-wt% normalization procedure requiring the entire matrix (all major elements) for quantification has been studied in great detail. Special attention was given to the accuracy of SiO_2 and some results for major element determinations using glass standards will be presented.

Keywords: imaging

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PLW-2 Laser-induced breakdown spectroscopy: the secret life of surfaces and other captivating insights

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Laser-induced breakdown spectroscopy (LIBS), one of the most active fields in analytical spectroscopy, is reaching a considerable level of maturity both in instrumentation and in analytical methodology and applications. Development of LIBS instruments with extended capabilities for energy dosage to the sample using ultrashort laser pulses has been undertaken which have permitted a better understanding of the underlying issues of LIBS – notably, laser interaction with matter, plasma dynamics and properties. The increased sophistication of laboratory methods permits LIBS to face analytical problems of remarkable complexity such as isotopic analysis. This lecture will present less explored aspects of LIBS, including the ultrafast phenomena occurring after laser excitation of surfaces and the ensuing onset of atomic and molecular emission and new measurement opportunities for extremely low masses.

Keywords: femtosecond laser ablation, LIBS, surfaces, single nanoparticle analysis

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KW-1 Atomic oncology: personalising cancer radiation treatments with LA-ICP-MS

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The standard treatment for most cancer patients with solid tumors is surgery followed by chemotherapeutic drugs, radiotherapy and/or enormously expensive antibody-based drugs. Drugs dissipate to normal as well as cancerous tissues and produce many adverse effects. By contrast, radiation is localized to the tumor-containing organ and importantly, there is differential sensitivity to radiation between different types of tumors.

It has been well established that certain types of bacteria such as *D. Radiodurans* are extremely resistant to ionising radiation. Daly **[1]** has suggested that *D. Radiodurans* exploits manganese complexes as antioxidants for protection of its proteins and DNA repair enzymes to impart protection against radiation and that proteins rather than DNA are the principal targets of biological action in sensitive and extremely resistance bacteria.

This presentation demonstrates that the same mechanism is responsible for radio-resistance and radio-sensitivity of human tumors. We imaged microarrays of various tumors known to be sensitive or resistance to radiotherapy by LA-ICP-MS. Resistant tumors such as melanoma had extremely high concentrations of manganese, whereas sensitive tumors such as seminoma had low concentrations of manganese.

LA-ICP-MS imaging of human tumor biopsies that are routinely used in all hospital and private pathology labs, in conjunction with other modalities, can help radiation oncologists to make more informed treatment decisions on patients with diverse tumor types.

Keywords: laser ablation, inductively coupled plasma mass spectrometry, manganese, radio, resistance, radio, sensitivity

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KW-2 New and emerging femtosecond laser sampling approaches in laser induced breakdown spectroscopy

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Laser ablation sampling encompasses complex phenomena spanning from the femtosecond time regime all the way to hundreds of microseconds, and includes among others, energy absorption, plasma formation and particle condensation. All these processes have direct impact on the optical emission signals and therefore analytical precision and sensitivity, because they control the plasma properties, expansion dynamics and chemical reactions in the plasma state. Additionally, each of these processes can vary widely depending on the laser sampling configuration. In this talk, we provide an overview of recent work on emerging ultrafast laser approaches that serve to improve spatial resolution, enable remote sensing of elements and isotopes, and preferentially enhance or impede chemical reactions for the formation of simple diatomic oxide molecules. Enabling laser technologies include femtosecond filaments, ultrafast optical vortex beams and femtosecond- induced weakly ionized air plasma channels as sampling sources for enhancing the precision of laser induced breakdown spectroscopy (LIBS) and laser ablation molecular isotopic spectrometry (LAMIS) measurements.

Keywords: ultrafast laser sampling, LIBS, LAMIS

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KW-3 Elemental speciation in biological and environmental samples involves natural nanoparticles and molecular species – new developments

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Elemental speciation has focussed in the last decades mainly on small molecular elemental species of toxic compounds such as mercury, selenium or arsenic. When high molecular forms of elements such as selenoproteins or metalloproteins are the focus of an investigation, then the authors are portraying this as metallomics study. Furthermore, when particles are formed and if they are in a nano-range, then the research has been described in the area of nanoscience. All these categorisation is not helpful when real samples of biological materials are considered. Examples using long finned pilot whales will illustrate that selenium speciation analysis might involve all aspects from nanoscience to metallomics and speciation. Other examples of new developments with regards to fluorine speciation will be presented.

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KW-4 Laser ablation 3D chemical mapping with X-ray lasers

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Laser ablation microanalysis has made major progress and improved the quality of the microsampling, and the spatial resolution, such to be able to map the elemental composition of a material in 3D. The ICP source is however limited in the range of elements (no H,C,N,O or S and so on) and provides no molecular information. Further, the spatial resolution is still too coarse for the analysis of thin films or is significantly damaging the irradiated material.

Therefore, researchers have tried to solve such shortcomings with the use of ultrashort pulses, with some variable results. An alternative approach, still subject of better fundamental understanding, is the one that implies the use of shorter wavelengths. Since the early works with frequency quadrupled or quintupled Nd:YAG or the excimer lasers, the lack of lasers of even shorter wavelengths did not permit any further advance. Aim of this talk is to present new results related to the use of X-ray lasers and compare the results with state-of-the-art systems. In particular, we will show results related to the nano-scale mapping without elemental or molecular restrictions.

Keywords: laser assisted plasma, X-ray lasers ablation, chemical mapping, nanoscale resolution

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KW-5 Mass spectrometry under the ice

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Polar ice cores are among the best archives of atmospheric composition of the past. Analysing the snow layers continuously deposited during centuries and millennia, it is possible to reconstruct the chemical composition of the atmosphere of our planet. Many chemical species are entrapped in gaseous or particulate phase into the snow and ice and thanks to sophisticated analytical techniques we are able to quantify their fluxes into the Earth's surface. In addition, ice caps sometime conceal enormous undisclosed sublacial lakes, buried under hundreds meters of ice, which preserve fossil liquid water since millions of years. The majority of chemical studies have focused on determining inorganic components, such as major ions and trace elements as well as on their isotopic fingerprint. The analytical techniques used in these cases are mostly based on ion chromatography and mass spectrometry *e.g.* using ICP-MS for trace element characterization and stable isotope mass spectrometry for isotopic fingerprinting. In this talk, I review the different methods for inorganic and organic compounds determination in deep ice cores from polar regions, discussing existing research and what is needed to improve knowledge. I will also introduce the problems of sampling, analysis and interpretation of the data in ice core science. Specific decontamination procedures, analytical methods with low detection limits ($ng.L^{-1}$ or lower), fast analysis time and low sample requests need to be developed in order to ensure a good time resolution in the archive. This talk highlights the great potential for inorganic and organic compounds to be used as proxies for anthropogenic activities and natural processes and will discuss future trends in research and opportunities in the ice core analysis.

Keywords: inorganic mass spectrometry, organic mass spectrometry, ice cores analyses

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OW-01 Simple modeling of LIBS plasma parameters for extraterrestrial applications

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LIBS has been proven very useful for in-situ geochemical analysis on the Martian surface **[1]**. It has also been proposed for future missions to explore other bodies of the Solar System *e.g.* **[2]**. For this reason, it has become more important to understand the capabilities and challenges of LIBS under atmospheric conditions that are different from Earth. There is also a high interest in calibration-free LIBS (CF-LIBS) due to the highly versatile measuring conditions in planetary exploration.

In this study, we have developed a method to assist the analysis of LIBS spectra acquired under different atmospheric conditions corresponding to different extraterrestrial mission scenarios. The method is developed from first principles and without resorting to measurements on calibration standards, similar to CF-LIBS **[3]**. Our approach follows from the same theory and assumptions as the standard approaches of CF-LIBS, such as the construction of Boltzmann plots, but many labor intensive steps are automated.

Assuming an optically thin plasma in local thermal equilibrium (LTE) with assumed distributions of electron density and temperature, a linear relationship exists between the intensities of the atomic emission lines and the elemental concentrations. Our approach is to set up a system of linear equations between the extracted integrated peak intensities, in a given spectrum, and the theoretically predicted peak-intensities by the Saha-Boltzmann equation.

From this system of equations, the concentrations are solved semi-analytically by minimizing the residuals between the peak-intensities. The minimization is repeated using different simply parameterized functions of the electron densities and temperatures, *i.e.* the plasma parameters.

We evaluate the applicability of the method to data acquired under different atmospheric conditions. Moreover, we investigate the consequences of different assumptions and distributions of the electron density and temperature to the results and discuss the limitations of the approach.

Keywords: calibration, free LIBS, laser-Induced breakdown spectroscopy, plasma parameters

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OW-02 An automated single algae ICP-TOF-MS approach for the investigation of metal uptake in single diatoms

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Diatoms are located at the bottom of the food chain. Thus, toxicological relevant metals taken up by diatoms can possibly accumulate within the food web and cause harmful effects. Diatoms are a common test system in ecotoxicology. Toxicological effects weaken the growth of algae which is by default investigated by means of fluorescence detection - diminished fluorescence compared to a non-exposed control group indicates an effect. On basis of the expose concentration as well as obtained fluorescence data potential threshold exceedance in *e.g.* surface waters is assessed.

However, this approach does not allow for the determination of "real" accumulated metal concentration in diatoms. Common approaches are based on microwave-assisted digestion and elemental analysis via *e.g.* ICP-MS, ICP-OES or AAS. But, with regard to low absolute metal- content in algae, this strategy is only feasible in case of availability of a high biomass.

To tackle this problem, alternative, complementary approaches are highly needed. Within the last years, SP-ICP-MS for nanoparticle as well as single cell analysis turned out as a powerful technique to analyze metal contents as well as size distributions on broad size range (nano- to low micrometer scale). But, common ICP-MS systems do not allow for multi-element detection within single particle/cell events **[1,2]**. Thus, simultaneous MS detection devices are needed - just recently, ICP-TOF-MS experienced a revival **[3]**.

Within our recent work, we developed an automated sample introduction system based on a HPLC system used as flow injection device on-line with single particle ICP-TOF-MS for multielement analysis in single algae (diatoms). Two different diatom species (*cyclotella meneghiniana*, *thalassiosira pseudonana*) were exposed to several, environmentally critical elements (Cu, Zn), essential trace elements (Si, Fe, P) as well as nanoparticles (Fe-NPs). Algae were exposed for one week. The developed setup allowed for a fast, automated and high sample throughput single algae analysis. On basis of our large dataset a correlation of ecotoxicological effects with the exposed metal concentration was successfully achieved.

Keywords: single algae analysis (diatoms), single algae ICP-TOF-MS, automated flow injection ICP-TOF-MS, simultaneous multielement analysis

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OW-03 ^{57}Fe-enriched iron oxide nanoparticles – long term fate and cell tracking determined by means of LA- ICP-MS and MRI

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Magnetic resonance imaging (MRI) is already established since the early 1980's and is an inherent part of medical imaging techniques. In case of insufficient contrast of different tissues, the usage of various contrast agents is possible. Especially in the last few years, contrast agents based on gadolinium (GBCA) gained unfortunate publicity due to recent research results indicating the persistence of these contrast agents in the brain. Contrast agents based on iron oxide nanoparticles (IO-NPs) are alternatively used substances to enhance the contrast during an MRI examination.

In this study, the biodistribution of IO-NP contrast agents was analyzed. Because of the high natural iron background, ^{57}Fe-enriched IO-NPs were used to distinguish between the natural iron and iron from the nanoparticles. Various organs of healthy mice (liver, kidney, spleen and brain) were scanned at various time points after injection of the contrast agents with MRI (*in vivo*) first and were then analyzed with laser ablation coupled to inductively coupled plasma mass spectrometry (LA-ICP-MS, *ex vivo*). For cell tracking experiments, inflammation-inducing pellets were inserted under the skin. ^{57}Fe IO-NP uptake by cells of the anti-inflammatory system was analyzed with LA-ICP-MS.

The quantification of iron was performed by external calibration based on matrix-matched gelatin standards. In this project, the two isotopes ^{56}Fe and ^{57}Fe were quantified specifically in consideration of the natural isotopic ratio and mass bias of these isotopes.

In addition to the spatially resolved results gained from the LA-ICP-MS experiments, homogenized organ samples were analyzed by means of ICP-MS to determine statistically relevant results from all various sample types.

Enrichment of the ^{57}Fe IO-NPs was detected in all analyzed organs by quantification and by changes in the ratio from ^{57}Fe to ^{56}Fe in comparison to naive organs. Highest concentrations were found in spleen and liver. The distribution patterns changed over the different time points especially in the spleen samples. High ^{57}Fe concentrations in border regions of the inserted pellets indicate the uptake by cells of the anti-inflammatory system.

Keywords: bioimaging, la-ICP-MS, MRI, contrast agent

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OW-04 Assessing legacy pollution and new inorganic contaminants in complex environmental samples using ICP-MS based techniques

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Heavy metal contamination still represents a major adverse threat for many coastal and marine ecosystems within highly populated catchment areas because of their inherent toxicity, vast sources, persistence and non-degradability. Despite the ongoing reduction of emissions of such contaminants into the environment, the coastal zones of the North Sea still belong to the most impacted ecosystems worldwide. In particular, the ongoing evolution of coastal zones into industrialized areas, e.g. due to extensive shipping or the construction of offshore wind parks within the framework of the ongoing energy transition in Europe even boosted the release of either known, but also of various new contaminants into the marine environment. In the past, elemental analysis of complex environmental samples, using ICP-MS, was often restricted to the analysis of a few, well known heavy metals such as Cr, Ni, Cd, Hg or Pb, in particular due to interference or sensitivity related issues.

Nowadays, due to changing industrial processes and product portfolios also other elements such as the REEs beside PGEs and TCEs also new element species indicate an increasing release into the environment. As a result, it is mandatory to include the entire periodic table into such evaluation, to allow a better understanding of the current pollution status of heavy metals in such complex coastal ecosystems, which is of significance for public health concerns beside the overall future sustainable development and management of the coastal zones.

In consequence, new analytical approaches in terms of elemental as well as element species analysis beside suited data evaluation strategies are urgently needed and have to be developed, to identify the sources, fate and behaviour of contaminants within the different environmental compartments.

This contribution will focus on some recent developments covering the field of ICP-MS based elemental, element speciation and non-traditional stable isotopic analysis and their application within the context of large scale environmental studies on the interactions of river catchments and coastal zones. Here the focus will be in particular on the recent possibilities arising from the application of ICP-MS/MS for interference handling as well as on new hyphenation approaches for ultra trace analysis of contaminants at sub $ng.L^{-1}$ levels, in order to evaluate systematically the emission load caused by anthropogenic activities within river systems and the coastal zone as well as to develop suitable tracers for these processes.

Keywords: ICP-MS/MS, REE, trace elements, environment, speciation

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OW-05 Rules of thumb for fast and high quality LA- ICP-MS imaging in single pulse or continuous scanning mode

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There are several avenues and schools of thought how to generate good LA-ICP-MS element maps. Especially with the recent advance of "fast" LA cells and the use of (simultaneous) ICP-TOF-MS detectors, instead of the commonly used quadrupole (scanning) ICP-MS detectors, the playing field has changed radically. The conventional approach of *continuous line scanning* will be compared to the more recent approach of *single pulse analysis*. ICP-MS analysis in the former case is performed by sampling a steady stream of aerosol particles (generally with overlapping laser pulses), whereas in the latter case single pulses are integrated (generally with non-overlapping laser pulses). This presentation describes the strengths and weaknesses of these LA-ICP-MS imaging approaches based on the quality of the output image derived as a function of the instrumental variables at several concentration levels. A computer simulation model for virtual LA-ICP-MS imaging and objective image quality metrics were used to select the optimal mapping conditions for fast and high-quality imaging with minimal blur and maximal S/N. Experimental imaging of decorative murrina glass validated this optimization strategy and led to the development of a simple template for the best instrumental settings.

Keywords: imaging optimization, image quality, image quality metrics, simulation, experimental validation

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OW-06 Improving mass balance for size resolved elemental speciation of environmental water samples using field flow fractionation online with ICP-MS

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Particle bound as well as dissolved nutrients and pollutants are key parameters to understand environmental water systems including for example algal blooms in lakes. Established techniques address total elemental contents, dissolved species such as phosphate and in recent years an increasing number of field flow fractionation studies focusing on the nanoparticulate and colloidal fraction using ICP-MS detection.

The latter technique provides a qualitative and quantitative overview on particle bound metals from the low nanometer size up to several hundred nanometers with minimum requirements for sample preparation **[1]**. However, this technique excludes the dissolved fraction from detection due to loss from the separation channel through the membrane. In addition, limitation for upper particle size has been reported in the range of about 2 to 3 µm or even lower depending on elemental composition.

The broad particle size distribution of suspended particulate matter in lake water samples from China shows about 60% of particle number below 5 µm, but this fraction accounts only for about 7% of particle volume and thus mass. To overcome this challenge we investigated the upper particle size limit in more detail trying to increase the particle fraction detectable by FFF online with ICP-MS. Complementary, we explored novel strategies for monitoring and quantification of the dissolved fraction in order to achieve improved mass balance and a complete overview on the elemental fractions in the sample.

Keywords: field flow fractionation, mass balance, dissolved fraction, particle size limit

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OW-07 Laser ablation ICP-MS in analytical recycling of iron-gall ink indicator papers

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Iron gall inks were commonly used between the Vth and XXth centuries; they were made from iron salts (usually: green vitriol/iron(II) sulphate) and tannic acids from vegetable sources (mostly: gall nuts from oaks). A water-soluble polymeric organometallic compounds (including ferrous tannate complex) were formed, then mixed with binding media solutions for easy application onto a paper during writting or drawing actions. With time, the inks darkened due to oxidation of Fe^{2+} to Fe^{3+} and formation of ferric tannate. Depending on the chemical composition of paper suport (fillers and binding media) as well as proportions of the substrates used to produce inks not all of Fe^{2+} ions might be transformed to Fe^{3+}. After centuries various inks indicated different corrosive activity towards cellulose present in the paper suport. This phenomena is so common that it was given a name "*ink corrosion*". A special bathophenanthroline indicators specific for Fe^{2+} ions was proposed for conservators to assess the risk of destruction of manuscripts due to corrosion **[1]**. These non-bleeding indicators are available for the every-day use in a conservation practice and easily applied to inked areas which eventually release Fe^{2+} changing the color of indicators. Based on the response of the indicator chemical treament is proposed for each diagnosed item. The truly efficient conservation treatment should fit to the individual chemical composition of each ink and for this purpose analytical recycling of the used bathophenanthroline indicators was proposed.

Chemical diversity of historic inks reflected by the indicators was investigated by means of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Elemental variety of historic inks was evaluated based on results of mapping of elemental distribution (Mg, Al, Sc, Ti, Cr, Mn, Fe, Co, Cu, Zn, Ag, Cd, Sn, Hg, Pb) over the indicators which were previously kept in contact with different documents covering the timespan of 400 years (from XVIth to XXth century). Experiments were carried out using LSX-213 (CETAC, USA) with ICP-MS (NexIon 300D, Perkin Elmer, USA). Application of Principal Component Analysis allowed to distinguish main groups of historic inks which should be subjected to a specific chemical treatment during conservation processes aimed to remarkably slow down the kinetics of corrosion reactions.

Keywords: laser ablation, archaeometry, ICP-MS

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OW-08 Traceability of oxidized mercury measuremnt in air

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The direct measurement of gaseous Hg(II) has become a major focus of international research programmes for continuous source emission and ambient measurement and monitoring. These measurements are dependent on the availability of reliable Hg(II) gaseous reference standards and materials to assess and verify the quality of data. In most existing methods for mercury measurements, it is typical that different oxidized mercury species are reduced to the detectable elemental form in order to be quantified. Reliable Hg(II) reference gases are needed to quantify this conversion and to assess the ability to quantitatively transfer especially the reactive Hg(II) through the entire measurement system. The EURAMET has approved a new project in the framework of the European Metrology Programme for Innovation and Research related to comparability of oxidized Hg measurements – MercOx. The overall objective is a traceable on-line and sorbent-based measurement for the monitoring and control of mercury in its different oxidized forms in emission sources and in the atmosphere in order to achieve significant improvements in measurement uncertainty. To meet this objective, the following steps are necessary: (i) to develop, establish and implement a traceable calibration methodology for the most important oxidized mercury species, especially for $HgCl_2$; (ii) to study, develop and compare different methods of measuring oxidized mercury; (iii) to compare, develop and establish conversion and sample transportation methods employing traceable reference standards developed for Hg(0) and oxidized mercury and (iv) to apply the developed methodologies in order to test and validate new and existing methods for on-line mercury measurement under field conditions by employing developed gas standards or generators. Main achivements so far and challenges will be presented .

Keywords: oxidized mercury, air, calibration, comparability

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OW-09 Quantitative assessment of spatial inhomogeneity of major and minor uranium isotopes in solid nuclear materials using LA-MC-ICP-MS

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Nuclear forensics, aiming at identifying the origin of nuclear material found out of regulatory control, is based on reliable analytical data. The isotopic composition of uranium is a key signature for characterising uranium bearing materials. In this context, the abundance of the four isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U was determined accurately in solid nuclear materials using a UV 213 nm ns-laser ablation system coupled to MC-ICP-MS **[1,2]**. The quality of the uranium isotopic measurements was assured by regular analysis of the two certified isotopic reference materials CRM U-030 (pressed to a pellet, 3 wt% ^{235}U) and CRM U-125A (4 wt% ^{235}U, sintered UO_2 pellet) as well as by comparative TIMS analysis. Spatial information on the uranium isotopic composition of several seized low-enriched UO_2 pellets and one metal containing depleted U was obtained through line scan analysis while moving the laser beam across the sample surface for several minutes. The ablation of a few thousand 5 µm spots was performed at a frequency of 4 Hz and at a speed of 20 $\mu m.s^{-1}$ allowing detailed insights into the isotopic (in-)homogeneity of the investigated specimens. This spatially resolved information cannot be obtained using bulk techniques such as gamma spectrometry, TIMS or solution-based MC-ICP-MS. The shape and width of frequency histograms of the measured U isotope ratios shed additional light on the homogeneity of the samples. Descriptive statistical parameters such as skewness and half-width of the corresponding normal distribution allowed straightforward classification of the generated datasets into homogeneous and inhomogeneous samples. This data, in turn, provided useful indications on the production process of the investigated materials that are of considerable value for nuclear forensics.

Keywords: MC-ICP-MS, laser ablation, uranium isotopes, inhomogeneity, nuclear forensics

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OW-10 Monitoring of priority and emerging contaminants in the open ocean

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To identify the impact of pollution and to protect the human health and the health of marine ecosystems, the survey of marine environment is of primary importance. Even though many contaminants show only low concentrations in the environment, they are of great concern due to their specific chemical properties and effects even at low dose, which makes highly sensitive analytical methods mandatory. Recent developments in multi element and isotopic analysis of selected priority and emerging contaminants opened new possibilities to conduct large scale monitoring studies. Comparability of monitoring data is mandatory for evaluating spatial and temporal contamination trends and is only achievable if only good quality measurement results are considered. Only reliable measurement data obtained with validated analytical methods, having stated uncertainty and demonstrated traceability to the common system or references, can be compared.

Accurate and precise quantification of trace contaminants in the open ocean and seawater samples remains a difficult analytical task, due to low analytes concentrations (typically below 1g.L^{-1}), very complex matrix (3.5% TDS) and possibility of contamination during sampling or sample preparation step.

This contribution will focus on the development of analytical procedures for the determination and monitoring of selected priority and emerging contaminants in seawater. The elements (Cd, Cu, Fe, Pb, Mn, Co, Ni, Zn, REEs, U, Th, Pu) at trace and ultra-trace level were determined with high resolution sector field inductively coupled plasma mass spectrometry (HR- ICP-SFMS) after applying relevant pre-concentration and matrix separation sample preparation strategies.

A validation approach in line with the requirements of ISO/IEC 17025 standard and Eurachem guidelines were followed in the development of all proposed analytical methodologies. The total uncertainty associated to each result was estimated and all major contributions to the combined uncertainty of the obtained results were identified. Demonstration of traceability of obtained measurement results to the common system of references is also presented.

Determining pollutant sources is another major problem when dealing with contaminants in the environment. Effective environmental regulation can only be accomplished if contaminant distributions can be unambiguously linked to known processes or sources. Analytical methodology for the application of lead isotopic ratios as a powerful tool for environmental monitoring of the open ocean will be also discussed.

The potential of the developed analytical procedures is demonstrated by analysis of seawater form different regions of the world.

Keywords: monitoring, priority contaminants, emerging contaminants, open ocean, isotope ratios, ICP-MS

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OW-11 Development of laser based procedures for stoichiometry analysis of ternary boride thin films

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The application of thin films via physical vapor deposition (PVD) offers enormous potential in modifying the surface of bulk materials to reach the requirements of various scientific and industrial applications. Traditional materials for hard protective coatings include nitrides and carbides. A rather new class of hard materials are borides of transition metals, which allow to combine hardness with ductility as well as chemical resistance. However, the mechanical/chemical properties of such boride coatings are closely linked to their elemental composition, control of the PVD process is therefore a prerequisite for the preparation of coatings with tailored properties. A difficult task since elemental fractionation effects can occur during sputter deposition, optimization of the PVD procedure requires therefore accurate determination of derived thin film composition.

Measurement of the composition of boride thin films is challenging, boron is hard to measure with X-Ray diffraction and X-Ray fluorescence analysis, the need of appropriate matrix matched standards or certified reference materials for quantitative determinations limits the applicability of most other solid sampling techniques. In literature, also liquid analysis of sample stoichiometry is reported, for conversion of the solid material into a liquid procedures such as acid digestion, fusion or dry ashing are applied. These methods are well established but require a significant investment in sample handling, are prone for sample contamination and/or analyte losses and provide only information on the average composition of the material.

Here we present two laser based approaches for the characterization of boride thin films, enabling analysis of sample composition but also homogeneity. Ternary boride thin films based on tungsten diboride alloyed with tantalum, aluminum of vanadium were prepared by PVD, determination of sample stoichiometry was accomplished using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser induced breakdown spectroscopy (LIBS). For signal quantification the concept of self-aliquoting micro-grooves has been applied, which represents a further development of the "dried-droplet-approach" described in literature. This method allows to easily adapt matrix composition and dopant levels in account to the needs of the application thanks to the vast variety of available liquid standard solutions. Thus, with this approach, the need of certified reference materials with similar composition could be circumvented. Conventional wet chemical analysis was used for verification of derived LA-ICP-MS and LIBS data, confirming accuracy and applicability of the proposed laser based procedures.

Keywords: LA-ICP-MS, LIBS, thin film analysis, stoichiometry

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OW-12 Investigating arsenate uptake in C. reinhardtii cells using single cell ICP-MS and its effect on lipid remodelling using ambient MS

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Mass spectrometry has been one of the most prevalent techniques for studying biological populations, offering superior capabilities for both atomic and molecular level studies through metallomic and lipidomic analyses.

Concerning metal determination, the most common method for quantitating the metal/metalloid content of a cell population involves acid digestion and analysis of the resulting digest through the use of ICP-MS. However, this method cannot give us a complete picture regarding the uptake of metals by cells as the mean metal content may not reflect a possible cell-to- cell variation, in addition to the fact that the accuracy of this value will depend on how accurately the cells have been counted. The potential of single cell (SC)-ICP-MS analysis with respect to metal determination in individual cells is being investigated, and so far results have been promising **[1-4]**. In terms of lipidomic analysis through the use of mass spectrometry, conventional methods require that cells be lysed in order to apply lipid extraction protocols, which may in turn induce lipid degradation. The use of ambient MS to investigate the lipid profiles of cells may overcome the afore-mentioned limitation.

In this work, the arsenic content of individual *Chlamydomonas reinhardtii* cells following their incubation in three non-lethal arsenate (As(V)) concentrations was determined using SC-ICP- MS. In addition, the effect of As(V) on cell lipid content was also conveniently determined using ambient mass spectrometry, *i.e.* desorption sonic spray ionization (DeSSI)-MS **[5]**. The purpose for using these analytical techniques in combination is to avoid time consuming sample preparation steps and allow for cell analysis, either of single cells or multiple cells, in a state that is as close as possible to their native state. In addition, it is our intention to evaluate both As uptake and lipid profile changes in a more unified approach, possibly identifying potential interactions more readily from minute numbers of cells.

Keywords: metallomic and lipidomic analyses, SC-ICP-MS, ambient MS, *Chlamydomonas reinhardtii*

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OW-13 Multi-energy calibration and sample fusion as alternatives for quantitative analysis of high silicon content samples by laser-induced breakdown spectrometry

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The direct analysis of high silicon content samples by laser-induced breakdown spectrometry (LIBS) is a good alternative, since the decomposition of samples with refractory characteristics is not an easy task. However, poor precision and difficulty in performing quantitative analysis due to particle size effects, heterogeneity and matrix interference are challenges which need to be overcome. An interesting strategy to minimize the problems associated to sample heterogeneity and particle size is the use of borate fusion process for sample preparation. In turn, a suitable calibration strategy is required to overcome matrix interference enabling quantitative measurements. Recently, a novel calibration strategy termed as multi-energy calibration (MEC) was proposed aiming at to simplify the calibration process and to make matrix matching feasible. By considering the simplicity of MEC and the capability to circumvent the matrix interference, this work deals with the evaluation of this strategy associated with borate fusion for analysis of geological samples. The MEC-LIBS method's accuracy was evaluated by determining Al, Fe and Ti in NIST SRM 679 (Brick Clay). MEC calibration involved preparation of two fused glass beads: (i) a mixture of sample (NIST SRM 679) and blank (SiO_2) and (ii) a mixture of sample (NIST SRM 679) and the standard (NIST SRM 2703). Although good linearity (R2) was achieved on the MEC curves, it was found an unsatisfactory agreement between the analytical results and certified values, with relative errors around 30%. It is known that Fe content in glass samples causes a strong absorption band in the UV region making the absorption of laser energy (266 nm) dependent on Fe concentration. To minimize the absorption effects caused by Fe, since Fe content in fused glass bead 1 is about 2-fold lower than in bead 2, and improve the accuracy of the method, boron, present in the flux, was used as internal standard (IS) for spectra normalization. Compared to MEC-LIBS method, IS-MEC-LIBS method showed better agreement between the analytical results and certified values, with relative error lower than 7%. These results showed that MEC associated with borate fusion is a simple and efficient method for LIBS calibration, but the success of this approach is only possible using internal standardization to minimize absorption effects caused by Fe content.

Keywords: LIBS, borate fusion, internal standard, MEC

The presenting author is a laureate of EWCPS-2019 PhD student grant

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OW-14 You've got to be kelping me! Determination of ^{129}I /^{127}I in kelp samples using ICP-MS/MS

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Proper thyroid function is crucial to the regulation of hormones, growth and development. Iodine is an element that is essential to proper thyroid function. Many foods are naturally rich in iodine, kelp being one of them. ^{129}I is produced by the fission of uranium atoms during the operation of nuclear reactors and by plutonium (or uranium) in the detonation of nuclear weapons. Therefore, the concentration of ^{129}I and the ratio of ^{129}I to ^{127}I changes significantly depending upon the geographic region (10-11 to 10-2). Accelerator mass spectrometry and instrumental neutron activation analysis are the most common analytical techniques for the determination of $^{129}I/^{127}I$, yet ICP-MS/MS offers certain advantages over these techniques. Several samples of kelp were collected from local stores in Seattle, USA covering a range of source locations from China, Iceland, Japan, Korea, and the USA. Concentrations of iodine in these samples ranged from 5-710 $mg.kg^{-1}$. The ICP-MS/MS instrument was optimized to achieve the highest signal for iodine while keeping the ^{129}I background at the minimum. At the optimal conditions, different iodide and iodate standards obtained from the USA consistently provided $^{129}I/^{127}I$ between 4 x 10-11 and 2 x 10-10. Due to the high sensitivity of the ICP-MS/MS instrument, ^{129}I /^{127}I as low as 10-12 can be measured in sample solutions containing as little as 20 ppm iodine in only 10 minutes. Lower concentrations of iodine in some kelp samples required preconcentration before analysis and, for these samples, an ion chromatography system was used for the on-line preconcentration of iodine. Results from different kelp samples are presented along with a discussion of challenges related to obtaining accurate $^{129}I/^{127}I$ using different ICP-MS technologies.

Keywords: ICP-MS/MS, isotope ratio analysis, iodine, kelp, preconcentration

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OW-15 Feasibility of nanoparticle-enhanced laser ablation inductively coupled plasma mass spectrometry

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Nanoparticles (NPs) applied to the surface of some solids can increase signals in inductively coupled plasma mass spectrometry (ICP-MS). Drops containing 20 and/or 40 nm nanoparticles of Ag and/or Au were deposited on metallic and ceramic/glass samples and, after being dried, both the samples treated with NPs and plain targets were ablated by one pulse per spot. The laser ablation ICP-MS (LA-ICP-MS) signals were enhanced for metallic samples modified with NPs in comparison to signals produced at the plain, untreated surface. Maps of LA-ICP-MS signals recorded for several laser fluences show that the NP-induced signal enhancement exceeds even 2 orders of magnitude for metallic samples. No enhancement was achieved for nonconductive samples. This enhancement is limited to the peripheral annular region of the dried droplet area where NPs are concentrated due to the "coffee stain" effect. Ablation crater profilometric inspection revealed a more uniform material rearrangement over the NP-treated surface compared with the ablated plain target. However, besides a smoother crater bottom, no other evidence of an NP- enhancing effect was noticed, although an increased ablation rate was anticipated. Limits of detection dropped by 1 order of magnitude for the minor elements in the presence of NPs. Observed phenomena depend only on the NP surface concentration but not on the material or size of the NPs. An electron microprobe study of the collected ablation aerosol has shown that aerosol particles consisting of target material are aggregated around the NPs. The hypothesis is that such aggregates exhibit better transport/vaporization efficiency, thus enhancing signals for metallic samples. A detailed study of the suggested mechanism will be continued in ongoing work.

Keywords: laser ablation, inductively coupled plasma, mass spectrometry, nanoparticles

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OW-16 Studies of biosorption of nano and ionic forms of gold by green algae in surface water by HPLC-ICP- MS

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Metal-based nanoparticles have attracted increasing attention in scientific, industrial and commercial applications. Gold nanoparticles (Au-NPs) are widely applied in electronics, sensors, solar cells and catalysis, as well as in medicine for radiotherapy, cancer therapy or as drug carriers. Nanogold is often used as a component of food supplements and cosmetics. Due to increasing applications of nanomaterials in daily life, their emission into environment has been recently observed. Speciation analysis of nano and ionic forms of metal is essential when assessing the potential impact of nanoparticles on human health and the environment. Analytical techniques for the simultaneous determination of these forms in different matrices (consumer products, biological and environmental samples) are still required.

This work presents the study of gold biosorption by green algae *Acutodesmus obliguus*. The conditions for incubation of algae with species of gold (ionic Au and Au-NPs) were optimized, next the efficiency of biosorption of different gold species by algae cells was examined in Milli-Q water and surface water. The transformation of Au species during incubation process carried out in different media was observed. High performance liquid chromatography was used for the separation of nano and ionic forms of gold in this work. The separated species were determined by inductively coupled plasma mass spectrometry with using 8800 ICP-QQQ spectrometer (Perlan Technology).

Keywords: nanogold, biosorption, speciation, HPLC-ICP-MS

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A career history of laser ablation for chemical analysis

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How do you take a simple interest and turn it into a > 37 year career – find an purpose and convinve funding agencies! It's way cool to shine a laser on a material and see the tiny little spark (plasma). But, what to do with it? Well, as we know today, it is a great way to address a critical need within the world of chemical analysis – direct solid sampling without chemical dissolution. We came up with a name for the process – laser ablation! Sounds exciting (pun intended). Over the past fifty-plus years, laser ablation (LA) has been developed into a mainstay technology for direct solid sampling in analytical chemistry. The driving forces include rapid analysis, no acid digestion, spatial resolution and more. These attractive features has helped propel LA over other technologies for imaging analysis, especially because laser ablation sampling does not require vacuum and can be applied to any sample matrix.

Laser ablation is the sampling process not the analysis; a short-pulsed laser beam removes mass (sampling) for subsequent analysis. Nicely so, the laser sampling process can be optimized separately from optimization of the detection modality. The ablated mass is first heated into a luminous optical plasma at the sample surface that is spectroscopically measured (LIBS – Laser Induced Breakdown Spectroscopy) for elemental and isotopic content. Our new technology LAMIS (Laser Ablation Molecular Isotopic Spectroscopy) measures isotopes in laser plasmas at atmospheric pressure from molecular emission band spectra in addition to atomic and ionic line spectra. To date, we have demonstrated LAMIS by measuring B, C, H, D, Sr and other isotopes. For some isotopes, we have achieved < 0.1% precision with sensitivity in the ppm range.

As the plasma cools, the mass condenses to a fine aerosol which can be transported to an inductively coupled plasma (ICP) for sensitive and precise isotopic analysis. Research has shown over the years how laser wavelength and pulse duration influence ablation behavior and therefore analytical performance. Optimization of LIBS and ICP detection depends on the measurement requirements. The ICP with mass spectrometry (ICP-MS) is ideal for trace analysis of isotopes, especially for the heavier elements. LIBS is ideal for analyzing major concentrations and light elements, including O, N, H and the halogens. These two detection modalities complement each other nicely. Optical emission from the luminous plasma monitored simultaneously with the ICP- MS detection provides complementary elemental and isotopic analysis of the sample, with every laser pulse.

For imaging analysis, laser ablation with simultaneous ICP-MS, LIBS and LAMIS offers the ability to measure every element/isotope with fine spatial resolution. In addition, because LIBS and LAMIS are all-optical technologies, they are suited for spatial analysis at remote standoff distances. Conventional focusing of laser beams for distance is reliant on the size of the aperture. However, with femtosecond laser pulses, non-linear absorption processes allow the beam to form guided filaments, distance mainly dependent on the laser energy and pulse duration. These filaments can be used for ablation of a sample at a distance. By coupling femtosecond –filaments with LAMIS (F2-LAMIS), we have measured elemental and isotope ratios of samples at distances up to 70 meters (distance limited at this time to open-path space in our laboratory). The talk will provide a personal overview of my career experience with the understanding and development of laser ablation sampling with LIBS, LAMIS and ICP-MS for chemical imaging and analysis, from the first measurements in 1982 through today.

Keywords: laser ablation, LIBS, LAMIS, chemical imaging

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WP-1 Nano Secondary Ion Mass Spectrometry (NanoSIMS) for nanoparticle and trace element imaging in mammalian cells

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Nano secondary ion mass spectrometry (NanoSIMS) is a scanning ion technique that can analyse solid surfaces to produce elemental and isotopic images in 2D and 3D at the sub-micrometre scale. The sputtering of a focused positive or negative primary ion beam (with Cs^+ or O^- ions) in the sample surface produce secondary ions that are subsequently analyzed by a mass spectrometer under high vacuum. The NanoSIMS technique allow the chemical imaging of almost all elements in the periodic table (from hydrogen to uranium), and their stable isotopes, with a lateral resolution below 50 nm combined with high sensitivity.
NanoSIMS can be applied to a variety of samples in the fields of environmental science, biology, material science, toxicology and geology. It is especially relevant to analyze the distribution of macronutrient and trace elements at the sub-cellular level in cell biology in order to investigate biochemical functions, as well as metals and nanoparticles biosorption and bioaccumulation processes. Two specific studies will be presented to illustrate the potential of this technique:

(1) It was applied to study human lung cells exposed to barium sulfate nanoparticles. $BaSO_4$ nanoparticles are used in different industrial products and their inhalation may have an impact on human health through their absorption in lungs. Nanoscale imaging of exposed human lung cell cultures demonstrated intracellular accumulation of $BaSO_4$ and enabled furthermore the subcellular localization of individual nanoparticles.

(2) It allowed imaging of the phagocytosis of salmonella bacteria by murine macrophages, in order to further elucidate the involvement of trace elements such as Cu and Zn in this physiological process.

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WP-2 LA-ICP-MS study of Ag nanoparticle transport in a 3-dimensional *in vitro* model

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We have applied laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with subcellular resolution as an elemental mass microscope to investigate the distributions of Ag nanoparticles (Ag-NPs) in a 3-dimensional multicellular spheroid (MCS) model. The production of MCS has been optimized by changing the seeding cell number (500 to 40,000 cells) and the growth period (1 to 10 days). Incubations of MCS with Ag nanoparticle suspensions were carried out with a concentration of 5 mg.L^{-1} for 24 hours. Thin-sections of the Eosin stained MCS were analyzed by elemental mass microscopy using LA-ICP-MS to image distributions of ^{109}Ag, ^{31}P, ^{63}Cu, ^{66}Zn and ^{79}Br. A calibration using NP suspensions was applied to convert the measured Ag intensity into the number of particles being present in each analysis spot. The number of NP determined ranged from 30 up to 4,000 particles in an enrichment zone. The particle distribution was clearly correlated to the ^{31}P, ^{66}Zn and ^{79}Br and was localized in an outer rim of proliferating cells (confirmed by DAPI) with a width of about two-single cell diameters. For the highest seeding cell number NPs were only detected in this outer rim, whereas small molecules as for instance ^{79}Br and ^{109}Ag ions were detected in the core of the MCS as well. Aniline blue staining demonstrated that this outer rim was enriched in collagen structures in which fibroblast cells were embedded and a thin-membrane was visible which separated the core from the biological active cell layer functioning as biological barriers for NP transport. In this presentation, we will show the possibility of using this 3-dimensional model for toxicological and medical applications.

Keywords: imaging, LA-ICP-MS, silver nanoparticles, multicellular spheroids, fibroblast cells

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WP-3 Complementary bioimaging by means of LA-ICP- MS and MALDI-MS - Detection of gadofluorine P in mouse heart tissue after myocardial infarction

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Coronary heart diseases like myocardial infarction (MI) are the most prevalent cause of death in the world. Diagnosis of MI is mostly made by electrocardiography (ECG) or by determination of biomarkers like cardiac troponin. Magnetic resonance imaging (MRI) in combination with contrast agents could be another approach. Usage of Gd-based contrast agents for MRI examination is already established in daily clinical practice. Since most contrast agents are distributed systemically, it is of great importance to develop target-specific contrast agents to detect clinical changes already in early stages. In this projec,t the affinity of gadofluorine P, a novel Gd- based contrast agent, to infarcted tissue after MI was analyzed with MRI and two different analytical techniques (*ex vivo*).

B6 mice with differently progressed myocardial infarction were examined with MRI after intravenous administration of Gadofluorine P. After examination, all mice were sacrificed and their hearts were removed. Tissue sections were prepared and the samples were analyzed with two complementary imaging techniques. Laser ablation coupled to inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to quantify Gd in a spatially resolved manner in murine heart tissue using external calibration with matrix-matched standards based on gelatin. Matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) was used to confirm the distribution of gadofluorine P on a molecular level and to visualize morphologic tissue characteristics by endogenous molecules like heme *b* or phosphatidylcholine.

The combination of LA-ICP-MS and MALDI-MS as complementary imaging techniques is a versatile approach to localize and to quantify the gadolinium concentration originating from the administration of gadolinium-based contrast agents in infarctional heart tissue and healthy myocardium. A significant enrichment of gadofluorine P in infarctional tissue compared to healthy myocardium was found as well as higher accumulation in more advanced stages of MI. The distribution of gadolinium detected with LA-ICP-MS match with the distribution of the gadofluorine P ligand detected by means of MALDI-MS.

Keywords: complementary bioimaging, LA-ICP-MS, MALDI, GBCA

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WP-4 Gadolinium in human brain sections and co- localization with other elements after macrocyclic GBCA administration

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Macrocyclic gadolinium-based contrast agents (GBCAs), that are known for their very good safety profiles, are currently under investigation for their depositions in certain tissues *e.g.* bone and brain.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been used to map the depositions of gadolinium in human histologic brain sections and to correlate these with other elements following the administration of macrocyclic GBCAs.

Post mortem tissue sections of the dental nuclei of three patients were measured: one patient was injected with a GBCA (macrocyclic Gadovist®) 2 weeks before dead (patient Gd_1), one received Gadovist® 4 weeks before dead (patient Gd_2), and one was without GBCA application as control.

High Gd signals were found in the dentate nucleus of the patient that died 2 weeks following GBCA administration. A section of the patient with Gadovist® administration 4 weeks before dead showed minimal Gd signals slightly above the control sections without GBCA application. The digestion and quantification experiments have confirmed the high and relatively low amounts of Gd in patient Gd_1 and Gd_2, respectively. The LA-ICP-MS measurements revealed the co-location of high amounts of Gd, Fe, Cu, and P indicating a related accumulation mechanism of these elements.

LA-ICP-MS demonstrated deposition of Gd in human brain tissues with intact blood brain barrier and its correlation with other elements.

Keywords: gadolinium based contrast agents, GBCA, human brain, laser ablation inductively coupled plasma mass spectrometry, LA-ICP-MS.

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WP-5 Laser ablation ICP-MS for simultaneous quantitative imaging of iron and ferroportin in hippocampus region of human brain tissues with Alzheimer's disease

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Alzheimer's disease (AD) is a chronic neurodegenerative disorder leading to a progressive decline in cognitive functions and the development of dementia. Ferroportin (FPN) is a transmembrane protein that transports Fe from the inside to the outside of the cell. It was reported that FPN may bind to amyloid precursor protein to facilitate neuronal Fe export and that disturbances in these processes may be implicated in AD, causing neuron death by high Fe intracellular levels **[1]**. Unfortunately, the low concentrations of FPN in the hippocampus region make difficult its detection by conventional immunohistochemistry (IHC) methods.

The objective of this work is to localize and correlate the amount of Fe and FPN in brain tissue sections, particularly in the hippocampus (CA1 region) from healthy control (HC) and AD patients. To achieve this goal, highly sensitive analytical tools are required. In this vein, ICP-MS is being used in life sciences for trace element determination, enhancing the understanding of the role of proteins in biological systems. The analytical capabilities of ICP-MS are extended by the use of laser ablation (LA) sampling for direct analysis of solids, showing a huge potential for bioimaging studies. LA-ICP-MS allows not only the imaging of metals but also of biomolecules. In this later case, maps of specific proteins can be obtained in biological tissues after an IHC protocol with metal-labelled antibodies, constituting an interesting alternative to commonly used fluorescence detection.

Concerning FPN, an IHC procedure based on the use of Au-NCs bioconjugated with the specific primary antibody (Ab) *via* carbodiimide crosslinking is presented for the specific localization of FPN distribution in the hippocampus region. An improved synthesis procedure is presented in this work to obtain Au-NCs with better size homogeneity as compared to those previously employed **[2]**.The proposed methodology was applied to 5 mm thick brain tissue sections: 4 HC and 4 AD sections were selected as a proof of concept. Additionally, the FPN absolute quantitative distribution obtained by the proposed LA-ICP-MS methodology was compared to FPN localization provided by a semi-quantitative method commonly employed in IHC.

Keywords: ferroportin, Alzheimer's disease, gold nanoclusters, immunohistochemistry, quantitative imaging, laser ablation ICP- MS

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WP-6 Bioconjugated gold nanoclusters as labels in quantitative imaging of metallothioneins in ocular tissues by LA-ICP-MS

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Laser ablation (LA) coupled to inductively coupled plasma mass spectrometry (ICP-MS) is currently regarded as a powerful inorganic tool for solids trace element and isotopic analyses. Two of the most interesting features of LA-ICP-MS for elemental analysis are its high sensitivity and lateral resolution, allowing the direct mapping of the sample surface. On the other hand, the combination of immunoassays (based on the specific binding of antibodies with their corresponding antigens) with LA-ICP-MS can facilitate multiparametric analyses through elemental labelling, allowing the direct mapping of proteins in biological tissues.

In this context, the use of metal nanoclusters (NCs) as labels is a promising approach for biomolecules analyses: the ratio "number of metal atoms/size" in a NC is very high as compared to a polymeric label because it does not contain carbon or other non-metals, so higher amplification can be achieved with a smaller size (each NC can have more than 500 metal atoms with typical diameters of 2-3 nm) **[1]**. For this reason, use of metal NCs as elemental labels results in an innovative strategy to determinate the antigen distributions. Moreover, these metal NCs can be fluorescent, offering possibilities for multimodal imaging (through fluorescence and MS analysis) in the same tissue section.

Concerning protein analyses, a further challenge for protein imaging studies in biological tissues is related to the opportunity offered by MS-based techniques to obtain not only the protein distribution but also absolute quantitative information through elemental-labels **[2]**. In this communication, a method for absolute quantitative imaging of proteins (metallothioneins, MTs) in ocular tissues by LA-ICP-MS was developed. This method is based on the use of Au-NCs bioconjugated with antibodies that recognize specifically the localization of MT1/2 in human retina sections. External calibration based on Au standard-spiked gelatin sections was carried out. A stoichiometry of Au-NCs/available antibody of 1:1 was obtained and the high amplification provided by Au-NC labels allowed for obtaining the distribution of MT1/2 in the neurosensory retina layers by LA-ICP-MS. Experimental results were successfully corroborated by a commercial ELISA kit for MT1/2 in dissected human retinas from *post mortem* donors. It is important to note that the developed quantification strategy is of general application to other antibodies and other metal-labels, thus opening new avenues for the quantitative imaging of specific proteins in varied biological tissues.

Keywords: gold nanoclusters, immunohistochemical analysis, proteins, quantitative bioimaging, laser ablation
ICP-MS.

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This work was supported by project CTQ2016-79015-R by Agencia Estatal de Investigación (Spain) and FEDER. B. F. acknowledges her research contract RYC-2014-14985 to the Spanish Ministry of Economy and Competitiveness through "*Ramon y Cajal Program*" and L. A. and H. G. acknowledge financial support from "*Fundación Rafael del Pino*" and "*Fundación Cristina Masaveu Peterson*".

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WP-7 Isotopically-enriched tracers and ICP–MS methodologies to study zinc supplementation in single- cells of retinal pigment epithelium in vitro

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Age-related macular degeneration (AMD) is a progressive neurodegenerative eye disease where oxidative damage to retina and the retinal pigment epithelium (RPE) as well as inflammatory-mediated processes contribute to its development and progression. Clinical studies support the use of Zn supplementation, in combination with vitamins and antioxidants to reduce the progression of AMD. However, how Zn supplementation helps to slow down the progression of AMD is not precisely understood. Therefore, the potential roles of Zn in AMD and its protective effects or deleterious interactions are being investigated.

Laser ablation (LA) coupled to ICP-MS is currently regarded as a powerful tool for direct trace element and isotopic analysis of solids. Among the most interesting research areas for LA- ICP-MS, we can find the elemental imaging of biological tissues and last advances show that LA- ICP-MS can be an excellent tool for obtaining images of cells. In this vein, while conventional nebulization ICP-MS analyses provide an average concentration value for the bulk of cell cultures, LA-ICP-MS allow obtaining spatially-resolved analysis of the single-cell. Furthermore, although isotope pattern deconvolution (IPD) mathematical tool has been previously employed by MS to determine the contribution of individual mass spectra in mixtures of different "isotope patterns", it has not previously used combined with LA-ICP-MS for individual cells analysis.

In this work, the capabilities of LA-ICP-MS combined with IPD mathematical tool have been explored for molar fraction imaging in human RPE cells (HRPEsv) treated with different enriched stable isotope tracers of Zn supplements in the form of sulphate and gluconate. Interestingly, cell analysis by the proposed LA-ICP-MS methodology permits the localization of Zn within the cell and simultaneously allows for differentiating the endogenous contribution of Zn from the exogenous one. Furthermore, it is important to note that the developed strategy is of general application to cells subjected to supplementation studies, thus opening new avenues for the molar fraction imaging of exogenous tracers in biological samples (*i.e.* providing a more complete understanding of the bioavailability of exogenous compounds in the treated cells).

Keywords: retinal pigment epithelial cells, ICP-MS, multiple linear regression, enriched stable isotopes, laser ablation imaging

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WP-8 Thulium spiked gel for internal standardisation in LA-ICP-MS bioimaging: quantitative elemental distribution of uranium in kidney tissue

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The quantitative analysis of trace metals in different organs or cellular structures is a topic of emerging interest for the assessment of toxicological risk. The kidney is recognized as a major site for uranium accumulation able to induce renal toxicity. Due to its heterogeneous distribution within the tissue, the quantification appears to be of significant interest. Mass spectrometry imaging (MSI) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been employed for mapping and quantify uranium in histological tissue sections of mouse kidney. Samples were immediately immersed into a PFA solution during 24h, OCT embedded and stored at -80 °C until cutting in cryostat and mounting in gel covered glass slides. Sample preparation (tissue section thickness) and laser conditions were carefully optimized to assure the complete ablation of the sample matrix.

This works presents the development of internal standard correction methodology based on doped gelatine. In order to correct matrix effects, lack of tissue homogeneity and instrumental drift, a thulium (Tm, internal standard) spiked 10% (*m/v*) gel was prepared and deposited on the top of glass microscope slides. The reproducibility and homogeneity of the deposited gel was assessed by ablating several areas (0.5 x 0.5 mm, *n=20*) in which Tm was recorded. For quantification purposes, matrix-matched laboratory standards were prepared from a pool of mouse kidneys by dosing each level with different concentration of uranium. In the same way, several quality control (QC) samples were synthetized to prove the accuracy and precision of the analytical method. The unspiked tissue was used for blank control. The concentrations were verified by conventional liquid ICP-MS after acid digestion. These standards were cut and mounted onto glass slides in the same way as the samples.

Thulium spiked gel was demonstrated to be adequate for compensation of instrumental drifts during measuring time and matrix effects, which improves the quantification of elemental distributions and allows a trustworthy comparison of experiments performed at different times. The proposed analytical bio-imaging approach was successfully applied for quantification of uranium of kidney samples. The comparison of the calculated average concentration obtained by LA-ICP-MS and the results obtained after liquid ICP-MS analysis were in good accordance.

Keywords: laser ablation ICP-MS, bioimaging, uranium, kidney accumulation

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WP-9 Application of laser ablation inductively coupled plasma mass spectrometry for investigation of Li, Mn, Co and Ni deposition patterns on carbonaceous anodes in lithium ion batteries

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The state of the art lithium ion battery (LIB) consists of a lithium transition metal oxide (LiMO_2; M = Nix, Coy, Mnz (x+y+z = 1)) cathode, a carbonaceous anode and non-aqueous electrolyte, respectively. As the performance of the LIB technology is rising constantly, one of the major challenge remains in the form of capacity loss with continuous cycling, induced by complex aging phenomena **[1]**.

Transition metal dissolution (TMD), arising from the degradation of the cathode material, is still believed to be a major contributor to the overall capacity fade. Dissolution in the electrolyte and subsequent deposition of transition metals on the anode surface can negatively impact the protective properties of the solid electrolyte interface (SEI), resulting in ongoing electrolyte reduction and thus lithium loss, resulting in additional capacity loss **[2]**.

In order to improve the understanding of different influence factors on TMD and lithium loss, suitable analytical methods need to be applied. Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) offers the possibility to investigate lithium and transition metal deposition by providing spatial and depth resolved elemental information. Therefore, this work deals with the ongoing development of LA-ICP-MS application for the investigation of analyte deposition on aged carbonaceous anodes.

Keywords: lithium ion battery, LA-ICP-MS, transition metal dissolution

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WP-10 LA-ICP-MS as a tool for assessment of the accumulation of minerals and trace elements in the arterial wall samples with advanced atherosclerotic lesions

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The disturbances of concentrations and distribution of elements resulting in accumulation or depletion in tissues may lead or be a result of certain diseases. The accumulation of Ca, P and Mg in arterial wall, as well as risk factors of atherosclerosis (hyperlipidemia, hypercholesterolemia, hypertension) are associated with the formation of atherosclerotic plaque in the arterial wall.

The aim of the present study was to examine the distribution of elements in the arterial wall collected from patients with atherosclerosis obliterans (AO) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

In many studies the samples of arterial wall and atherosclerotic plaque were digested in strong inorganic acid and analyzed by solution nebulization techniques, like AAS, ICP-OES or ICP- MS. However, the step of digestion destroys the pattern of distribution of the analytes and the appropriate mapping technique should be used in order to obtain the spatial map of elements in the solid sample. In the case of human arteries with atherosclerotic plaque, the LA-ICP-MS method is particularly useful because it is capable to investigate not only the arterial wall or the plaque itself but also the conjunction of the two (which is up to several hundreds of μm wide) where the actual process of the plaque build-up/formation and calcification occur. The samples of the arterial wall with atheromatous lesions (100-500 mg) were obtained from patients with AO while vascular reconstruction (implantation of aorto-bifemoral prosthesis), placed on the plastic base and analyzed by LA-ICP-MS as a dried bulk sample after thorough and careful rinse with Milli-Q water. The samples were divided into two groups: containing the intact plaque, and the plaque with the surrounding soft tissues. The laser with the diameter of 150 μm traversed the sample line by line until the entire sample was mapped.

The main mineral components of the plaque are Ca, Mg, P, as well as some trace elements (Zn, Fe, Cu, Mn, Cr, Pb). The resulting maps of analyzed elements revealed the subtle differences in their distribution, as well as very large concentration of Ca, P, Mg and Pb in the atherosclerotic plaque in comparison to the arterial wall samples without the plaque. Calcification and formation of hydroxyapatite crystals within the plaque is the main reason of large minerals content. Increased content of essential trace elements in particular parts of the atheromatous arterial wall seems to be related to the presence of some metalloproteins participating both in the synthesis and degradation of the connective tissue (Zn in matrix metalloproteinases and their inhibitors), endogenous metal-containing antioxidants (Cu, Zn-SOD, Mn-SOD), Fe(III)-carrier and storage protein (transferrin and ferritin). It may be suggested that the differences in trace elements distribution found within the arterial wall may results from the structure and composition of its layers and the degree of the disruption due to atherosclerosis

Keywords: LA-ICP-MS, laser ablation inductively coupled plasma mass spectrometry, laser ablation, clinical samples, arterial wall, atherosclerosis, bioimaging, mapping, medicine

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WP-11 Investigation of the delivery of platinum bisphosphonates to hard bone tissue using LA-ICP-MS

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Bisphosphonates have been widely used to treat many types of bone diseases including osteoporosis and Paget's disease. They reduce the activity of bone degrading osteoclasts and thereby reduce the formation of weak or deformed bones. Furthermore, their efficacy in cancer therapy is currently being investigated. Combining cytostatic drugs and bisphosphonates offers a promising approach to treat bone metastases. The high affinity of bisphosphonates to bones can increase the uptake of these drugs by the bone tissue where the cytostatic effects are desired. To investigate if a higher uptake of bifunctional bisphosphonates is achieved compared to other cytotoxic drugs, a quantitative bioimaging method is necessary.

In this study, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to detect and quantify platinum in thin sections of mouse tibia. The mice were previously treated with a functionalized bisphosphonate. The resulting images were compared to microscopic images and distributions of calcium and phosphorous also recorded by LA-ICP-MS. Furthermore, X-ray fluorescence spectroscopy imaging was used prior to ablation to gain a further understanding of the sample.

The developed method can be used to visualize the distribution of platinum bisphosphonates in biological samples. This information can help to analyze and further optimize the delivery of cytostatic drugs via bisphosphonates and in turn improve drugs used in the treatment of bone metastases.

Keywords: LA-ICP-MS, platinum, bisphosphonates, bone diseases

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WP-12 Nanoparticles as tags for protein tissue analysis using laser ablation inductively coupled plasma and mass spectrometry

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Laser ablation with inductively coupled plasma is still more used in life science as biology and biomedicine and the utilization of metals and proteins determination simultaneously is also growing up. We have developed a new strategy of antibody labeling by nanoparticles which are composed of thousands of atoms and thus increase the sensitivity enormously and decrease the limit of detection (tens of picograms). The ability of simultaneous imaging proteins such as p53 and elements and their distribution in biological tissue (especially tumour) is presented in this work.

Keywords: nanoparticles, bioimaging, LA-ICP-MS, immunochemistry

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WP-13 Imaging of specific proteins by LA-ICP-MS

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The work is focused on development of the method which allows imaging of specific proteins. The concept is based on the interaction of antibody labelled with metal-based particle with its antigen. The metal-based particle are imaged by means of laser ablation with inductively coupled plasma mass spectrometry (LA-ICP-MS). The labelling of antigens is done by metallic nanoparticles. Each antibody is labelled by various metal-based nanoparticle.

Keywords: immunochemistry, LA-ICP-MS, protein analysis

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WP-14 Bioimaging of proteins in human ocular tissue sections by LA-ICP-MS using isotopically enriched silver nanoclusters as labels

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Degeneration of the retinal pigment epithelium (RPE) results in the build-up of extracellular deposits in the retina region of human eyes. The cell damage in the RPE can be attributed to a mechanistic set of events, including an intracellular release of free Zn and Cu, induction of Ca release and uncontrolled proteins aggregation. In this context, a neurodegenerative ocular disease denoted as age-related macular degeneration (AMD) can appear. AMD disease is the main cause of irreversible blindness among people 65 years or older and, it should be stated that nowadays there are not efficiency therapy treatments to stop this condition.

In this work, bioimaging studies of the proteins distribution in the retina region of human ocular tissue sections are proposed by laser ablation (LA) ICP-MS. LA-ICP-MS is characterized by easy sample preparation, multi-elemental detection with high sensitivity and a spatial resolution in the µm range. In order to perform not only elemental analysis of heteroatoms naturally present in the tissue sections but also protein analysis, an immunohistochemistry protocol was carried out using antibodies with metallic nanoclusters (NCs) as labels. Particularly, Ag-NCs synthesized using different Ag isotopes (natural abundance ^{107}Ag and isotopically-enriched ^{109}Ag) were selected as labels for multiplexing analysis of selected proteins.

Ag-NCs were synthesized with high and stable emission. Then, they were characterized by HR-TEM and ICP-MS to determine the particle size and number of Ag atoms per NC. On the other hand, the synthesis of isotopically-enriched Ag-NCs was also carried out. Their chemical and photoluminescence properties were studied and, finally, both Ag-NCs (natural abundance and isotopically-enriched) were bioconjugated to antibodies of two specific proteins related to AMD to study their distribution along different eye structures by LA-ICP-MS. The results of the proposed methodology can open the way to a quantitative analysis of elements and proteins involved in AMD, both using biological tissues and cell lines.

Keywords: RPE, isotopically enriched silver nanoclusters, AMD, LA-ICP-MS, multiplexing analysis

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WP-15 Super resolution reconstruction for bioimaging by LA-ICP-MS

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LA-ICP-MS has become a key instrument for investigating the chemical pathology of various diseases and conditions. There is a need for quantitative mapping with cellular resolution (< 10 µm). Here we present a new quantitative method for super resolution reconstruction by LA-ICP- MS. Image data was acquired by consecutively ablating layers and post-processed with methods frequently used by high resolution fluorescence microscopy. Parallel line scan layers were ablated offset by half the diameter of the laser spot size and orthogonally to the previous layer. Both standard and sample data were acquired using this method. The data sets for the layers were then processed using an in-house custom MATLAB script written using the Image Processing Toolbox, which produced either 2D or 3D maps from a multilayer acquisition. Scans acquired at 15 um spot size and a scan speed of 30um.s^{-1} had a theoretical image resolution of 3.25 µm in the xy-plane. This method allowed quantitative localisation at a cellular level for understanding elemental and metal- tagged protein distributions in health and disease.

Keywords: LA-ICP-MS, super resolution reconstruction, elemental bioimaging, 3D

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WP-16 Combination of high sensitivity and a fast full mass range scanning capability for imaging by laser ablation ICP-MS: performance of the high resolution ICP-MS AttoM ES

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For the past decades, interest in performing imaging with by laser ablation coupled with ICP-MS has grown in several area such as geology, bio medical, pharmacology… Recent improvements to laser ablation sample cells have prompted requests for even faster data acquisition for wide if not full mass spectra. Although high resolution magnetic sector ICP-MS has become the favoured instrument for many laser ablation applications due to the high sensitivities seen in dry aerosol sampling and the flat-topped peaks, it still has not been widely used for imaging purposes due to traditionally slower wide mass range scanning speeds compared to quadrupole ICP-MS.

Recent changes to the Nu AttoM ES have improved the speed for the closed loop control and a more powerful 200 V power supply provides a faster hysteresis loop of 400-800 ms. It has also been possible to increase the magnetic field ramping and fall-back speeds of the "linkedscan" mode to obtain spectra between lithium and uranium in 103 ms leading, meaning an acquisition rate of 9.7 Hz for full mass spectra. Combining the stable magnet field cycling with fast deflector scanning provides the ability to track the ions with deflectors in the opposite direction of the changing magnetic field and thus remain on the peak top for longer and improve the measurement duty cycle. The cycle time does not vary depending with the number of isotopes measured so when many isotopes are required, the time between data points can be significantly faster than a quadrupole ICP-MS.

In this work the interest of using this fast analysis mode for imaging purposes will be demonstrated on garnet and zircon.

Keywords: imaging, HR-ICP-MS, laser ablation, Nu Instruments, geology

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WP-17 Investigation of galvanic anode metal uptake in individual marine organisms (*Corophium volutator*) via complementary ETV-ICP-MS / LA-ICP-MS

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In regard to global warming and environmental protection, Germany is on its way to modify energy supply by using renewables. Offshore windfarms are and will be in the fore of these efforts and contributed in 2015 already about 8% of power produced via regenerative sources **[1]**. Actually, more than 1,000 turbines are already installed - further windfarms are planned or currently under construction **[2].** There is no doubt that renewable energy is the key technology for sustainable energy supply. However, the construction of windfarms entails an impact on marine ecosystems; thus, within a comprehensive life cycle analysis the impact of construction, operation as well as deconstruction of windfarms need to be taken into account.

Power plants as well as substations are installed on foundation structures made out of steel. Steel is prone to corrosion in aggressive media - especially in contact with seawater. To ensure a service life of at least 25 years for an entire off-shore wind farm, appropriate corrosion protection strategies are required. A strategy widely applied is using galvanic anodes. Galvanic anodes are made from less noble metals than steel. During operation they get dissolved to metal cations and deliver electrons to the steel. In case of corrosion protection in seawater, aluminum galvanic anodes doped with further trace metals are used and dissolve in the surrounding seawater. To guarantee corrosion protection for one pile for 25 years about 10 t of aluminum galvanic anodes are required. Thus, large amounts and a variety of metals are released into the seawater. Although a huge dilution effect is most likely, potential harmful impacts on a local scale are possible and widely unexplored.

Within the presented study, a model organism *Corophium volutator*, which is a mud shrimp found in the mudflats, was exposed to metal-doped seawater. Metals were chosen according to the common composition of galvanic aluminum anodes (Al, Zn, In, Pb). A possible metal uptake was investigated: (i) upon single organism ETV-ICP-MS analysis as well as (ii) bioimaging via laser ablation ICP-MS (LA-ICP-MS) **[3,4]** analysis to study the possible ingestion of metals.

ETV-ICP-MS as well as LA-ICP-MS turned out as a powerful complementary analytical tool in ecotoxicological tests: i) natural biovariability is accounted for, (ii) spatial resolution and bioimages allow for studying metal distribution within single organisms.

Keywords: marine organisms, single organism analysis, bioimaging, galvanic anodes, ETV-ICP-MS, LA-ICP-MS

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WP-18 Evaluation of ionization efficiency / sensitivity enchancement for a range of aerosol delivery systems for LA-ICP-MS

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In recent years, we have witnessed quite big advances in LA-ICP-MS. Several ablation cells with short washout times (few millisecond range) have been proposed and capabilities for fast imaging have been established. Different approaches are being proposed such as more traditional continuous scanning mode and more recent single pulse mode; in the latter the development of fast washout cell was playing a crucial role. In the view of shorter washouts, faster imaging times, smaller and smaller laser beam sizes are becoming possible, because the speed of imaging allows the analysis to be accomplished in a reasonable timeframe. With smaller beam sizes the amount of material ablated is diminishing and any enhancement in sensitivity is highly appreciated. Therefore, some aerosol delivery systems were tested and their influence on signal intensities were investigated. Some assumptions about the nature of signal enhancement (increased sensitivity) will be discussed, such as aerosol containment, improved ionization efficiency, aerosol flow paths, etc..

Keywords: laser ablation, fundamentals

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WP-19 Evaluation of the state-of-the-art LA-ICP-MS systems for elemental imaging of decorative glass object

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In this contribution, we present elemental images of highly decorated glass artefact – murina glass piece – that was imaged at three LA-ICP-MS setups, featuring different state-of-the-art cells and aerosol delivery systems (HelEx, HelEx with ARIS, cobalt with tube cell) interfaced to the same ICP-MS instrument. Murina glass piece was used as model sample in this work, as it features highly detailed surface elemental distributions. The sample itself can be used numerous times due to the fact that the decoration pattern is not changed after subsequent grinding/polishing.

Experimental conditions for the systems were used under the assumption of the "best possible image quality" for specific setup. With this starting condition, we evaluated different modes of operation, *e.g.*, continuous *vs* single shot, different number of overlaps/dosages, different laser beam sizes, element contents (concentation) and number of elements measured in one run. The resulting elemental images will be analyzed for the image quality, (noise, contrast, resolution) and total analysis time. Considerations for most efficient use of elemental imaging with these setups will be also discussed.

Keywords: LA-ICP-MS, imaging, image quality

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WP-20 Image analysis for 2D LA-ICP-MS bioimaging

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Bioimaging by 2D LA-ICP-MS results in elemental maps depicting the distribution of elements in a biological 2D sample. Additional information can be obtained by quantitative imaging where the amount of element per ablated area is determined. Further, it offers the possibility linking quantitative elemental distribution with structural properties of the sample, comparing distributions of various elements of interest, capturing kinetic effects on the elemental distribution and determining the biological variability of the elemental distribution using replicate samples. In this study, we quantitatively describe the elemental distribution in a 2D elemental map of a zebrafish embryo (ZFE), their variation among biological replicate samples and link these to structural information of the ZFE. ZFEs were exposed to a brominated chemical (naled) and subsequently analysed by LA-ICP-MS. Br was used as a marker to quantify uptake of the chemical. We determined the biological variability based on the total compound uptake and the intensity distribution model. A mean of 545±117 pmol Br/individual (corresponds to an enrichment of 282 compared to the exposure solution) was determined. Br distribution was referred to carbon content to account for the ablated material mass. The intensity distribution models of the LA-ICP-MS measurements of different individuals show the same modality and similar densities. The intensity distributions of 79Br are monomodal. However, intensity distributions of 12C are bimodal. The intensity distributions of carbon and bromine showed a significant shift of lower carbon intensities to higher frequencies and a frequency decrease of the lower Br intensities with exposure duration, respectively. The spatial distribution of Br in embryo tissue reveals comparatively high Br levels in the head of the embryo.

Keywords: zebrafish embryo, internal concentration analysis, quantitative chemical imaging

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WP-21 Of laser ablation and standards when analyzing hard biological materials

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Laser Ablation (LA) has become the most accepted method for direct sampling of solid material, especially for trace elemental analysis when used for inductively plasma mass spectrometry (LA-ICP-MS) and laser induced breakdown spectroscopy (LIBS). Nonetheless, the scarcity of matrix-matched standards or reference materials is an obstacle. This presentation will address newly developed standard materials to analyze biological materials. While different strategies have been applied in the last years such as using NIST glass SRMs, there is no SRM for hard biological materials, such as bones, teeth and hair in a solid form. In general, pellets of the powdered form of this material spiked or synthesized with a spike of the element of interest is the most common method for elemental analysis. But the density and compaction of these pellets do not match with the sample, which could falsify any calibration protocols.

In the case of teeth, bones or even calcified tissue, for which hydroxyapatite is the matrix, we propose the synthesis of reference hydroxyapatite standards which can be controllably spiked with different elements of interest. These materials have properties that mimic the calcified tissues they represent, thanks to the fabrication process that involves spiking during the HA synthesis and sintering of the pelletized powders.

We will also show a new protocol for the creation of keratin standards for the reliable and quantitative analysis of hair and fingernails. This approach relies on the cross-linking of a mixture of keratin and alginate which replicates the laser ablation conditions and allows the creation of elemental standards for such biological materials.

For both types of standards, analytical figures of merit will be shown and we will discuss the specific behavior of different elements in these standard matrices.

Keywords: standard reference materials, hydroxyapatite, keratin, biological materials

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WP-22 Quantitative determination of Cu via LA-ICP- MS in single triple negative breast tumor cells after treatment with a new Cu phosphine complex

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Triple-negative breast cancer (TNBC) is very aggressive and because of the lack of specific therapeutic targets and limited alternative treatments, it is still characterized by a poor prognosis. Patients diagnosed with this type of cancer have a significantly increased risk of relapse and death, stressing the need for new therapies. Metal complexes are playing an important role in the development of new and more effective anti-cancer drugs that induce less severe side effects and encounter less resistance. In recent years, literature has been addressing the potential of high- resolution elemental imaging *via* laser ablation-inductively coupled plasma-mass spectrometry (LA- ICP-MS) to investigate the uptake and spatial distribution of metal-based anticancer compounds, either approved or under investigation, in cell monolayers and tumor spheroids **[1]**. In this work, LA-ICP-MS was applied to study the cellular uptake and distribution of Cu in TNBC MDA-MB- 231 cells after incubation with a new Cu phosphine complex, which demonstrated a high cytotoxic potential against this cell line in preclinical studies. An Analyte G2 193 nm ArF* excimer-based LA system, equipped with the ultra-fast Cobalt ablation cell (Teledyne CETAC Technologies Inc., Omaha, NE, USA), was coupled to an Agilent 7900 ICP-mass spectrometer *via* the aerosol rapid introduction system (ARIS). Cu-spiked dried homogeneous gelatin droplets, prepared following the protocol described by **[2]**, were used as external calibration standards for the determination of Cu in single cells. Individual cells were quantitatively ablated by using a 30 µm diameter circular laser spot size and firing a series of shots at a high laser repetition rate. The instrument settings and data acquisition conditions were optimized to record the fast transient signals and the laser energy density was lowered in order to selectively ablate the cells from the microscope glass substrate. Furthermore, high-resolution LA-ICP-MS imaging was performed to visualize the Cu distribution in single cells. The results may contribute to a better understanding of the cellular uptake and accumulation of metal-based complexes in preclinical development.

Keywords: laser ablation, bioimaging, single cells

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WP-23 Data processing software for LA-ICP-MS

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The modern use of LA-ICP-MS often require hours of work after data acquisition, especially as the elemental imaging is becoming more desired. Relatively few non-commercial software tools are available to assist with this process.

The goal of this work was to create free, open source desktop application for fast processing and visualisation of mass spectrometric data. Our intention was to create simple, easy to use interface that will offer the first look on acquired data with no need of any preparation. This program was created using programming language python and the user interface was built on top of the standard library tkinter. Using PyInstaller program we created a one file executable, that can be used under Windows without the necessity of installing python or any other packages.

The program is aimed on data created with laser ablation inductively coupled plasma mass spectrometry. It is suited for a spot and line analysis as well as an elemental imaging. The data can be imported directly from mass spectrometry data acquisition as csv files. The program presents two ways of data evaluation; either calculating the mean of the peak values or using a peak integration. The automatic selection of the background and sample intervals from time resolved data is shown in the main window. There is an option to check every element in an interactive graph with highlighted background versus sample time view. This program also allows user to choose from 2 possible correction procedures; correction on internal standard and sum of oxides correction. Using a certified reference values, it calculates the content of measured elements. It is possible to export data at any step of the evaluation; data are exported into an excel sheet. It is also possible to create calibration curves. The intercept and the slope calculated in calibration window can be directly used for the creation of elemental maps.

Keywords: LA-ICP-MS, data processing, elemental analysis, elemental imaging

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WP-24 Assessment of ns-LA coupled to MC-ICP-MS for Fe isotopic analysis of meteoritic materials

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The characterization of extraterrestrial materials, such as meteorite phases and materials from sample-return missions, forms a major driver for the development of new analytical methods. Advanced direct solid sampling techniques at the mineral scale permit the characteristics of the materials to be correlated with the distribution of minerals and elements within the material, their isotopic composition, etc.. A multimodal approach, using a combination of semi- or non-destructive complementary techniques, is often required to obtain all necessary information on the specimen or mineral phase under investigation. In this presentation, the capabilities of nanosecond laser ablation coupled to multi collector inductively coupled plasma-mass spectrometry (ns-LA-MC-ICP-MS) for spatially resolved isotopic analysis of Fe in meteoritic materials will be discussed. This work was carried out using a combination of an Analyte G2 ArF*excimer-based LA-system with a Thermo Scientific Neptune MC-ICP-MS unit. The instrument settings and data acquisition conditions were optimized in order to adequately handle the transient signals obtained when using ns-LA for sample introduction. Instrumental mass discrimination was corrected for via matrix-matched standardization. Analytical protocols and data processing strategies will be discussed and figures of merit for relevant reference materials and actual samples presented.

Keywords: laser ablation, multicollector ICP-MS, stable isotopes, geological reference materials

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WP-25 Provenance determination of ancient Roman imperial coinage with tandem LA-ICP-MS/LIBS

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The currency system of the ancient Roman Empire was built around the usage of silver to be minted into coins. With its vast expansion under Emperor Trajan's rule (AD 98 - 117), it had access to a multitude of different silver mines to provide resources for the roman mints.

Previous studies have indicated that Trajan conducted a widespread coin collection initiative around AD 100 in order to dilute the silver content with copper, to provide funds for upcoming war efforts **[1]**. Additionally, it was observed that the Denari coins from his fifth consulate showed a significant increase of Pb contamination, which can be an indication for less refined Ag bullion or change of source material. However, aside from main and minor elements, no information about the trace elemental or isotopic composition was obtainable so far.

For the first time, a tandem LA-ICP-MS/LIBS approach has been applied to analyse 60 individual coins, ranging from Trajan predecessor Nerva to Trajan's sixth consulate, in order to gain a better understanding of the origin of the used silver ore. For this, lead isotope determination via ICP-MS was combined with simultaneous elemental fingerprinting via LIBS.

Keywords: tandem LA-ICP-MS/LIBS, tandem, LIBS, LA-ICP-MS

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WP-26 A LA-ICP-MS quantification strategy for the determination of particle-bound Hg as collected in air monitoring filters

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The anthropogenic presence of mercury within the environment is still of great concern, given the significant impact that mercury emissions can have on human health **[1]**. This is strongly evidenced by the large number of countries engaged with the Minamata Convention, which aims to reduce and, in a longer term, stop the release of Hg into the environment. However, there is a lack of traceability in the chain of mercury measurement used to support legislation, drive directives and enforce limits on emissions/release into the environment.

As part of the MercOx project (EURAMET-funded European Metrology Programme for Innovation and Research project to develop metrology capability for oxidised mercury), a LA-ICP- MS calibration strategy has been developed and evaluated as a high throughput alternative to acid digestion and ICP-MS analysis of particle-bound mercury collected on filter paper. This strategy employed the use of blank filter paper, gravimetrically spiked with mercury containing solutions, as matrix-matched standards. Such standards were *in house* characterised for Hg homogeneity using LA-ICP-MS and total Hg concentration by acid digestion and ICP-MS. Over-saturation of the standards with the Hg spike provided a relatively uniform radial distribution of mercury across the filter. As the radial distribution of the samples varied between collection locations, total integration of ^{13}C-normalised signals from sample and standards (corrected for ablation line length) were used for quantification. The average recovery (compared to Hg concentrations from digests) obtained for samples collected from the UK Runcorn area was 98.7% with an expanded uncertainty of 53.7% (k=2), to which the major contributing factor was the between line variation as a result of large signal variation from non-ablation particle liberation. This presentation will describe the advantages of the newly proposed method and existing related challenges and will propose a feasible approach to reduce measurement uncertainty.

Keywords: LA-ICP-MS, mercury, air monitoring filters

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WP-27 Improving accuracy and precision in LA-MC- ICP-MS

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The gold standard of analytical chemistry is complete separation of interfering elements from the isotopic system of interest, usually through sample dissolution and column chemistry. However, geological samples often crystallise during two or more growth events, necessitating the use of *in situ* analytical techniques such as laser ablation (LA) to preserve spatial resolution. The drawback of these techniques is the lack of any chemical separation procedures, which often necessitates one or more interference corrections to resolve the desired isotopic ratios. To achieve the best accuracy and precision under these analytical conditions, all isotopes of interest and potential interferents should be measured simultaneously, such as by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, voltages at the required masses can vary considerably due to different natural and/or radiogenic abundances, a particular problem when a major isotope of an isobaric interference must be calculated from a minor isotope. Accurate and precise determination of laser ablation isotope ratios therefore requires detectors which can cover the full dynamic range of interest, including Faradays with switchable resistors and secondary electron multipliers (SEMs) or Daly detectors, to ensure correct removal of interferences and minimise the uncertainty propagated through the interference calculations.

Keywords: laser ablation, multicollector plasma mass spectrometry

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WP-28 Adaptation and improvement of an elemental mapping method for lithium ion battery electrodes via of laser ablation inductively coupled plasma mass spectrometry

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Lithium-ion batteries, first introduced by Sony in 1991, still experience a loss in performance over time. Although the technology is state of the art in portable consumer electronics, widespread application in automobiles demands improvement beyond the current capabilities. Understanding deterioration processes and mechanisms (the so called aging) requires the examination of aged cells. As electrochemical cells and especially electrodes do not age homogeneously and electrochemistry in general is heavily dependent on surface properties, bulk analysis is not suitable for investigating these phenomena. However, the understanding of these aging phenomena in lithium ion batteries (LIBs) is a crucial factor for current and future LIBs. Even state of the art LIB systems show some degree of performance loss over time which has to be investigated. For example, changes in the distribution of lithium or transition metal deposition in the LIB can have a huge impact on the cycle and calendar life of cells. Therefore, we developed methods using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in order to visualize the distribution pattern of lithium and transition metals in lithium ion battery. Spatially resolved deposition patterns can help to understand the mechanisms regarding metal migration and lithium loss. For this, it is crucial, that the obtained images have a good resolution. Therefore, we adapted a method with a substantial reduction of time and resource consumption is preferred, while preserving an adequate resolution. Additionally, the optimized method was applied to the electrodes in order to visualize the distribution and deposition pattern, respectively

Keywords: LA-ICP-MS, lithium ion batteries, transition metal, lithium

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WP-29 Solid-spiking piking matrix matched isotope dilution laser ablation ICP-MS for simultaneous determination of cadmium and chromium in sediments

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Direct analysis of solid samples offers important advantages that overcomes most of the limitations of conventional methods, such as high consumption of reagents and generation of wastes, long sample preparation procedures and the risk of analyte losses and/or contamination. In this sense, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is one of the most powerful tools for elemental determination in solid materials. However, several limitations complicate its implementation in routine quantitative analysis as, for example, the limited availability of commercial calibration standards. Isotope dilution (ID) is nowadays one of the most promising approaches in this field to guarantee an accurate quantitation. In this sense, the use of matrix-matching standards has been proposed, which implies the addition of the isotopically enriched spike solution to each powdered sample to be analysed, requiring subsequent homogenization and drying for each solid sample to be analysed. This procedural approach is tedious and time-consuming. The synthesis of a unique isotopically enriched solid spike has been proposed **[1]**, avoiding the addition of spike solutions to the solid samples. This solid spike is then easily mixed with every sample by a simple and rapid procedure (homogenization in a mortar) and subsequently pressed to pellets.

In this work, a LA-ID-ICPMS procedure was developed to determine Cd and Cr in sediments based on the solid-spiking matrix-matched methodology. The effect of the variables affecting the laser ablation process was studied using a Plackett–Burman experimental design. Two drying procedures for the synthesis of the isotopically enriched solid spike were studied (rotary evaporation and freeze-drying) in terms of elemental distribution of the target elements in the pellets using Nested ANOVA and also considering the time efficiency. The measurement step was programmed to measure, in a unique sequence, Cd (low mass resolution) and Cr (medium mass resolution) in the same ablation line. Accurate results were obtained for the analysis of two reference sediments with certified total contents of Cd and Cr, with experimental/certified ratios around unity. Very good precision (calculated from three analysis using independent pellets) was achieved for Cd (2 % for SRM 1944 and 4 % for PACS-3) and for Cr (7 % for SRM 1944 and 10 % for PACS-3). Uncertainty estimation led to satisfactory values, between 10 % and 17 %, as relative uncertainties. The applicability of this approach was demonstrated by the analysis of marine sediments collected at the Northwest coast of Spain.

Keywords: solid spiking, isotope dilution, laser ablation, ICP-MS, cadmium, chromium, sediments

Acknowledgements

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WP-30 Accurate measurement of uranium isotope ratios in solid samples by laser ablation multi-collector inductively coupled plasma mass spectrometry

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Uranium isotopic composition is widely measured in nuclear materials for process and quality control purposes. If such material gets out of regulatory control (despite physical protection and nuclear safeguards), detailed analyses are required to assess the hazard, intended use and origin of the material. These measurements, often referred to as *nuclear forensics*, involve the comprehensive analysis of the material in question **[1]**. Destructive analytical techniques for U isotope ratio measurement, such as thermal ionization mass spectrometry or multi-collector inductively coupled plasma mass spectrometry offer unparalleled accuracy and precision. This is obtained, however, at the expense of significant effort for sample preparation and production of waste. Furthermore, a substantially higher quantity needs to be treated. The use of laser ablation with ICP-MS overcomes these shortcomings **[2]**. Another advantage is that LA-ICP-MS offers high spatial resolution and can therefore provide additional insights in inhomogeneity, which points at the production process and starting materials used.

A rapid method was developed for the direct measurement of U isotope ratios in solid nuclear samples **[3]**. Certified nuclear reference materials (CRMs) of different ^{235}U enrichments ranging from depleted to low-enriched uranium were used to validate the experimental results. The CRMs were provided as powders, from which pressed pellets were prepared to mimic U fuel pellets. Only approximately 5 ng of U per measurement is needed for the analysis, thus the analysed material remains macroscopically unaltered and the sample (specimen) can be kept as evidence, as archive or for further investigations (quasi-non-destructive). The measurement can be performed within a few hours, hence essentially shortening the analysis time and largely reducing the amount of radioactive waste. The developed method is a powerful tool for the examination of seized nuclear samples and for nuclear safeguards.

Keywords: laser ablation, MC-ICP-MS, uranium, isotope ratio measurement, nuclear forensics

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WP-31 Preparation and characterization of polymer- based multi elemental reference materials

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Reference materials are of special interest in analytical chemistry, especially for quantification of elements in samples, for quality management and for the validation of new methods.

The quantification of elements in solid based samples in contrast to liquid (digested) samples has the advantage of spatial resolution, which gives valuable information on the elemental distribution in samples. However, especially when it comes to biological samples, there is a lack of suitable, commercially available solid based reference materials in an appropriate range of elements and concentrations. The available reference materials (e.g. from NIST oder BAM) are mostly glass- oder metal-based and therefore not suitable for the quantification of softer tissue, as the matrix is not comparable.

For this purpose, reference materials with on polymer basis with a variety of 21 different elements were produced and characterized. Acrylic resin polymers and polymeric additives were used as a base and a multi-element oil-based reference material was introduced and homogenized in the base polymer. Reference materials in different mass fractions (10 to 300 mg · kg -1) were prepared. The real concentrations of these materials were analyzed with ICP-OES, whereas the homogenity was checked with LA-ICP-MS. Furthermore the layer thicknesses of produced polymeric layers were determined by light microscope.

Keywords: reference materials, polymer, LA, ICP, MS, calibration, solid state analysis

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WP-32 High Performance Thin Layer Chromatography coupled with LA-ICP-MS and LDI/MALDI-FTICR- MS to study asphaltenes

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Heavy fractions are considered to be the most problematic parts of crude oil. In fact, they contain large amounts of hetero elements (S), metals (V, and Ni) and polyaromatic molecules. These elements are poisoning the catalysts used in refining units. They must be extracted by expensive hydrotreatment processes. Information obtained on these hetero-elements and their chemical environment also referred as speciation, are important to improve treatment steps.

Vanadium and nickel in crude oil are mainly present as small polar molecules called porphyrins. These molecules remain preferentially in asphaltene (part of the crude oil soluble in toluene and insoluble in aliphatic solvent such as C7). This asphaltene part is composed of large polar and hetero-element containing molecules, having a capacity to self-aggregate. They could form aggregates between a few hundred Daltons to several hundred thousand Daltons. Some of these porphyrins could be easily accessible or trapped inside aggregates and become therefore refractory to hydrodemetallation treatment steps.

HPTLC is used for the separation of petroleum and heavy petroleum, so called SARA separation. In this study, HPTLC was used to separate asphaltenes in two fractions among which V, Ni and S containing molecules were detected by LA-ICP-MS. Moreover, LDI/MALDI-FTICR-MS was used for the identification of the molecules containing these elements.

Samples of asphaltene extracted with pentane (A C5) or heptane (A C7), asphaltene 2017 (A 2017, reference asphaltene produce for the Petrophase 2017 conference) and V and Ni reference porphyrins were separated by HPTLC. The HPTLC plates used are cellulose plates (HPTLC cellulose plate, MERCK, thickness: 0.15-0.2mm). Cellulose as stationary phase gives better signal than classically used silica in LA-ICP-MS and LDI FTICR-MS. A Dichloromethane 99.5%/ Methanol 0.5% mixture was used as mobile phase for the migration.

After migration, UV analysis was performed with a CAMAG TLC Scanner 4. A Laser ablation system (NWR 213 from electro scientific industry) was coupled to an ICP MS instrument (7700 series from Agilent) to determine the quantity of metal and sulfur. Moreover a FT ICR Bruker solarix (12 Tesla) instrument equipped with a MALDI source was used for the identification of molecule.

After the migration step, almost all the reference porphyrins migrated to the solvent front. The asphaltene sample split into two parts. One part remained at the application point and one migrated to the solvent front. It seems to appear that the point at the solvent front corresponds to the free porphyrins, and the other one could correspond to porphyrins trapped into asphaltene aggregates. FT ICR analysis will confirm this hypothesis.

Keywords: asphaltenes, petroleum, Heavy fractions, metals, HPTLC, LA ICP MS, LDI/MALDI FT ICR MS

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WP-33 Imaging artifacts in elemental bioimaging via LA-ICP-MS due to excessive fluence and poor tissue preservation

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Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is a well- established micro-analytical technique that is rapidly gaining importance in the field of elemental bioimaging, stimulated by the development of low-dispersion ablation cells, which greatly enhance sensitivity and sample throughput.1 In order to achieve high-quality images, the instrument settings and data acquisition conditions have to be carefully selected. van Elteren *et al.*2 described a major source of imaging artifacts (ripples) in 2D elemental images, generated by desynchronization between the laser repetition rate and the data acquisition rate of sequential scanning-type mass analyzers, *i.e.* quadrupole filter or sector-field mass spectrometer.

This study identifies additional sources of imaging artifacts in elemental bioimaging *via* LA- ICP-MS, caused by (1) an excessive laser energy density or (2) poor preservation of biological tissue. Applying excessive laser energy density can lead to fracturing and cracking of the tissue, resulting in the ejection of large particles and eventually, intense positive spikes in the elemental maps which compromise the image quality. This also applies to dried-out tissue sections caused by poor sample preservation. Provided that adequate attention is paid to the sample preparation and synchronization of the laser repetition rate and data acquisition rate, while the laser energy density is reduced to below 0.5 J cm-2, high-quality images can be achieved.

All experiments that will be presented in this poster were carried out using an Analyte G2 193 nm ArF* excimer-based LA system (Teledyne Photon Machines Inc., Bozeman, MT, USA), equipped with the recently launched ultra-fast COBALT ablation cell and hyphenated to a quadrupole-based Agilent 7900 ICP-MS unit (Agilent Technologies Inc., Tokyo, Japan) *via* the Aerosol Rapid Introduction System (ARIS). LA-ICP-MS imaging was performed on kidney tissue sections of animals which were administered with pharmacological doses of cisplatin, and were previously used to evaluate the nephrotoxic side effects of cisplatin, as described in Van Acker *et al.*3

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Keywords: LA, ICP, MS, imaging artifacts, bioimaging, selective ablation, COBALT

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WP-34 Energy density control for selective ablation of biological material from a glass substrate using a nanosecond 193 nm laser

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A prerequisite for reliable quantitative elemental imaging of biological tissue *via* LA-ICP- MS is the quantitative and selective ablation of a tissue section from the substrate, typically a standard glass microscope slide. Careful selection of the dosage (number of shots per position) and energy density is required to limit the amount of material removed from the underlying substrate, as co-ablation of substrate material which contains significant levels of the element(s) of interest could lead to a considerable signal background contribution and thus, erroneous results. At a laser energy density below the ablation threshold of a material (*soft ablation* regime), *i.e.* the laser energy density at which the coupling efficiency increases promptly, thermal processes, such as vibrational excitation, will lead to limited evaporation of particles only.5 A higher laser energy density above the ablation threshold (*hard ablation* regime) will increase vaporization due to phase explosion processes and result into the ejection of larger particles.5,6 The ablation threshold is determined by material-dependent characteristics, such as its thermal conductivity and attenuation length. In general, laser radiation with a shorter wavelength yields a higher coupling efficiency and lowers the significance of thermally relative to photochemically driven ablation processes.2 Since the ablation threshold of soda-lime glass is well above the ablation threshold of soft biological tissue, the laser energy density can be reduced to a value below the ablation threshold of glass in order to achieve *soft ablation* for glass and *hard ablation* for tissue. In this way, only negligible amounts of material will be removed from the glass substrate, even if the laser beam is directly interacting with the glass, *e.g.*, in the case of a cavity in the tissue or around the sample edges. This presentation will demonstrate the capability of a nanosecond 193 nm laser to selectively ablate kidney tissue from a SuperfrostTM soda-lime glass microscope slide substrate by controlling the laser energy density. In this manner, even the distribution of major elements of the microscope slide, *e.g.*, Ca and Si, can be revealed in kidney tissue, originating from a previous study described in Van Acker *et al.*7

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Keywords: LA, ICP, MS, selective ablation, ablation threshold, kidney tissue, bioimaging

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WP-35 Calibration methods for spatial determination of Platinum-based chemotherapy agents in tumor samples using LA-ICP-MS bioimaging

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Platinum (Pt) analogs are the main anti-tumor compounds used for treatment of cancer of distinct origins, even though their benefits remain limited for many patients. Patient-specific intratumoral heterogeneity may directly impact drug penetration and performance, so factors regulating Pt accumulation may act as biomarkers to predict patient response to therapy.

In contrast to classical Pt measurement methods (e.g. ICP-MS or FAAS) that do not allow the analysis of Pt spatial distribution, LA-ICP-MS techniques have been recently validated for spatial detection of Pt-based anti-cancer compounds throughout tumor sections in preclinical mouse model1,2. In this context, the intra-tumoral distribution of platinum, obtained by LA-ICP-MS imaging methods, allowed the evaluation of the clinical association between Pt distribution patterns and response to treatment in patients.

Accurate quantification of Pt uptake in tumor from patients previously subjected to platinum-based therapy requires proper calibration samples. These samples should have a known quantity of Pt homogeneously distributed at least in a representative large region, and should ideally behave, during the ablation and atomization/ionization processes, in a similar way as the tissues to be studied.

The present work explores the suitability of two potential calibration models applied to cancer tissue bioimaging using LA-ICP-MS: *Ex vivo platinum calibration method* and *Basement Membrane Extract (BME) platinum calibration method*. First approximation is based on a human tumor explants model, which *ex vivo* recapitulates the intra-tumoral complexity of cancer in patients and supports the evaluation of *in vitro* treatment efficiency with determined concentrations of chemotherapy. Freshly resected tumor samples from untreated cancer patients were sliced in equivalent pieces and treated *ex vivo* with increasing concentration of Pt (0 to 200μg/ml) during 48h. After tissue fixation, inclusion and sectioning, samples of 6 and 20 μm thickness were submitted to LA-ICP-MS to measure platinum uptake. The second method evaluates the accuracy of BME (Basement Membrane Extract) mixed with pre-determined quantity of Pt to calibrate platinum uptake measurement in tumor tissue. BME matrix is a reconstituted basement membrane preparation extracted from the Engelbreth-Holm-Swarm (EHS) sarcoma, a tumor rich in extracellular matrix proteins. BME resembles the complex tissular environment found in many cancers. Volumes of chilled liquid BME mixed with increasing concentration of Pt (0 to 5 μg/ml) were dispensed onto microscope crystal slides. Following polymerization, [Oxaliplatin/BME] mixtures were incubated during 72h in humidified atmosphere before submission to LA-ICP-MS measurement.

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Keywords: bioimaging, LA, ICP, MS

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WP-36 Depth profiling of UV-light degradation of modern art materials using LIBS

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In the fields of modern and contemporary art, the employment of materials such as synthetic polymeric binders and inorganic as well as Synthetic Organic Pigments (SOP) is constantly growing. However, the stability of these paint mixtures towards atmospheric environment and light irradiation is not yet clear. For this reason, the study of the degradation processes of these materials exposed to aging conditions is of significant interest.

Traditional methods for investigating degradation processes of polymers are FT-IR and Raman spectroscopy. However, these techniques can only be applied to surface regions and do not allow analysis of the elemental composition of the sample. Compared to FT-IR and Raman spectroscopy, LIBS offers direct access to elemental analysis and enables measurement of depth profiles. Additionally, characteristic regions in the LIBS spectrum can be used to identify and characterize molecular changes in the polymer.

In this work, different pigment and polymeric binder combinations were exposed to artificial UV aging, thus altering the samples. Depth profiles of these changes in the polymer network and influences on the pigments were analysed using LIBS and multivariate statistics.

From the industrial point of view, these results can be used to improve the quality and stability of synthetic materials. On the other hands, from the artistic point of view, the results can help the development of new suitable preventive conservation strategies.

Keywords: LIBS, polymers, arts, aging, degradation

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IWP-37 nvestigation of polymer degradation under corrosive conditions using tandem LA-ICP-MS/LIBS

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Polymers are widely used in the coating industry as protective layers for different materials. For certain applications, the polymer has to withstand and protect the underlying material from harsh environmental conditions such as high temperatures, exposure to UV-radiation and exposure to corrosive gases. To provide optimal protective properties, the polymer should not degrade under these conditions and should prevent alteration of the underlying material.

FT-IR spectroscopy can be used to investigate degradation of polymers. However, FT-IR spectroscopy can only be applied to surface regions and does not allow measurement of corrosion products derived from inorganic materials. Compared to FT-IR spectroscopy, tandem LA-ICP-MS/LIBS offers direct access to trace metal analysis as well as characteristic regions in the LIBS spectrum which can be used to analyze changes in the polymer network. Additionally, tandem LA-ICP-MS/LIBS enables the measurement of depth profiles.

In this work, different polymers were exposed to various corrosive conditions altering the polymer network. Depth profiles of these changes in the polymer network were analyzed using LIBS and multivariate statistics. Additionally, changes of the elemental composition within the polymer due to corrosion of the underlying material and the diffusion of the corrosive gases could be detected by combining LIBS with LA-ICP-MS.

Keywords: tandem LA-ICP-MS/LIBS, multivariate statistics, polymers, degradation

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WP-38 Laser-induced breakdown spectroscopy in analysis of building materials

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Analysis of building materials as concrete or asphalts is an important issue. Environmental protection must be taken into account during recycling. Another aspect is material properties for further use of the recycled building mixtures. Composition of these materials is studied with various analytical techniques. Content of both major and minor elements can be determined with e.g. optical emission or mass spectroscopy. Laser induced breakdown spectroscopy (LIBS) can be successfully employed for analysis of concrete and asphalt samples. It can replace some more complicated processes of sample decomposition prior to the analysis with inductively coupled plasma optical emission or mass spectroscopy (ICP-OES or -MS). The application of the LIBS technique on concrete and asphalt samples is demonstrated here. Because of the lack of calibration standards for LIBS, special effort is dedicated to the development of the standards and compensation of matrix effects. Limestone and cellulose matrices were used as a possible alternative to laboratory-made cement standards. The studied building materials are inhomogeneous. There could be a problem with selection of representative pieces for spatial and bulk analysis. Comparison of the results can then be a little bit complicated. Main constituents as cement or asphalt binder and stones show different response on the impact laser beam. Especially, soft asphalt shows lower microplasma emission and requires more corrections than concrete during a quantitative evaluation. Analysis of the sample picture and various internal standardization techniques were used to demonstrate their practical applicability to bring true information about the elemental composition. Reference bulk analysis with ICP-MS was used for comparison.

Keywords: LIBS, concrete, asphalt, ICP-MS, matrix effect, calibration, standard, standardization

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WP-39 Quantitative multielemental mapping of biological samples by laser-induced breakdown spectroscopy: a case study of pig tissues

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Trace elemental analysis and elemental mapping of biological samples can provide valuable information for diagnostic and fundamental research purposes. Such analyses are usually carried out by laboratory-based atomic spectroscopy methods that require liquid samples or by synchrotron- based methods (e.g. PIXE, NAA, XRF) that may directly work with solid samples. Unfortunately, these methods need an extensive sample preparation or are not easily accessible, therefore other, more practical and faster analytical methods are continuously sought for. One promising method is laser induced breakdown spectroscopy (LIBS), which offers a unique set of advantageous analytical characteristics including low detection limits, applicability to samples of any shape and physical form, no need for sample preparation, minimal destructiveness, no contact with the sample, possibility to analyse practically all elements in the periodic system, very fast analysis, etc.. LIBS can potentially also be used for chemical elemental mapping, with micrometer-range spatial resolution. In spite of the above potential, LIBS has scarcely ever been used in the literature for the quantitative elemental mapping of biological samples.

In the focus of the present work was the development of an analytical method which would allow the quantitative elemental mapping of thin sectioned biological samples. As test samples, six different pig tissue types (liver, brain, kidney, heart, lung, muscle) were chosen, partly because of their similarity to human tissues (thereby allowing the projection of the potential applicability of the method to medical or pathological problems), and partly because they are easily accessible from commercial sources.

The experimental conditions were optimized for the generation of the plasma as well as for the collection of emission spectroscopy data. The effect of the matrix on the analytical signal for the elements P, S, Na, K, Mg, Ca, Fe, Zn, Mn, Ni, Cu, was studied. Three different calibration approaches were tested with all tissues after grinding and homogenization. These approaches included univariate calibration using matrix-matched standards, univariate calibration based on gelatine-matrix standards, and finally multivariate pricipal component regression (PCR). The most reliable results were obtained with the PCR method. Validation of the results was carried out by ICP-OES (for Ca, Mg, K and Na) and by ICP-MS (for the other elements) after acid digestion of the tissue samples. After the successful calibration of elements, we demonstrated the application of the method for the collection of the quantitative elemental map of a 30 µm thin, 5 x 8 mm size pig brain sample section.

Keywords: LIBS, elemental mapping, biological samples

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WP-40 Composition and morphology analysis of bimetallic nanoparticules generated in a spark discharge plasma

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Nanotechnology has gone through a rapid advancement in the past 20 years. Its main aim is to prepare and analyze, and ultimately engineer objects with dimensions in nanometer size range. The synthesis method applied has a crucial impact on the characteristics of prepared nanoparticles (NPs). Nowadays, chemical synthesis methods are the most wide-spread thanks to their advantages (e.g. tunability, flexibility, no need for complex instrumentation, etc.). However, their demand for chemicals is high, they generate a significant amount of waste and, in many cases, the purity of the prepared products may be sub-optimal for certain applications. A suitable alternative is offered by physical synthesis methods as they are environmentally friendly, energy-efficient and are able to prepare high-purity products **[1]**.

One promising representative of physical NP synthesis methods is spark discharge generation. In addition to the above-mentioned advantages of physical methods, a spark discharge generator (SDG) also has a fairly simple design and a great potential for NP mass production **[2, 3]**. The principle of operation of SDGs is that a high voltage oscillating discharge is produced between two electrodes (favourably made of conducting or at least semi-conducting material). Erosion and vaporization of the electrodes are realized by the plasma created by the discharge. In result atomic vapor forms which is carried away by a gas flow. Finally, nucleation and coagulation processes produce nano-sized aggregates, which can be compacted to form spherical NPs. Utilizing the fact that different materials can be chosen for the two electrodes, it is possible to produce nanoparticles containing two or more elements (bimetallic nanoparticles, B-NPs).

Due to the novelty of utilizing an SDG for BNP synthesis, the effect of operating parameters (e.g. electrode polarity, gap size) on the prepared nanoparticles' characteristics (composition, size distribution, etc.) has not been discussed in detail in the literature so far. Our study aims at revealing the correlation between these by utilizing inductively coupled plasma mass spectrometry (ICP-MS), transmission electron microscopy (TEM) and scanning mobility particle sizing (SMPS) for bimetallic nanoparticles like Au-Ag, Au-W, Au-Cu, Cu-Co.

Keywords: nanomaterials, LIBS

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WP-41 Real-time sample surface height control and intensity normalization for laser-induced breakdown spectroscopy analysis of edible salts

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We investigated the feasibility of a simple laser-induced breakdown spectroscopy (LIBS) analysis method for quantification of Mg and Ca in edible salts. The LIBS instrument assembled with a compact diode-pumped solid-state laser and a non-gated handheld spectrometer. For sampling, a piece of filter paper was dipped in the aqueous solution of salt and dried to be analyzed by LIBS. Due to the low pulse energy of the DPSSL (270 microjoule.pulse^{-1}), a slight deviation of the sample surface height (SSH) from the laser focus readily decreases the laser fluence on the sample surface below the plasma ignition threshold. To tackle this issue, the SSH variation was monitored and compensated in real time during the laser ablation. Initially, the SSH was located at the focus of the objective lens. This position was monitored by a small digital microscope viewing the optical fiber end surface on which the plasma plum was imaged through two collection lenses. While the sample stage translated to collect spectra from different areas of the sample surface, the SSH was adjusted to locate the plasma image at the initially optimized position. Also, inhomogeneous distribution of dry residues on the filter paper deteriorates the analysis precision. To correct this, the peak that consists of the Na(I) and C(II) lines at 568 nm was employed as a reference signal for intensity normalization of the analyte Mg(II) and Ca(II) lines. For edible salt products, the normalized intensities were well calibrated to the concentrations of Mg and Ca determined by inductively coupled plasma optical emission spectroscopy. Our results indicate that the simple LIBS device and analysis method can be applied for on-site salt quality assessment.

Keywords: laser-induced breakdown spectroscopy, sample surface height control, intensity normalization, edible salts

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WP-42 Optimization and detailed spectroscopic characterization of an improved spatial heterodyne laser-induced breakdown spectroscopy setup

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The spatial heterodyne detection principle has a great potential in spectroscopy. It has an optical setup similar to that of a Michelson interferometer, with the mirrors replaced by diffraction gratings positioned at fixed, equal distances from the beamsplitter and are slightly tilted. The resulting interference pattern is recorded by a digital camera and the spectrum is recovered by using Fourier transformation. Although spatial heterodyne spectroscopy (SHS) was initially developed for astronomical and satellite-based atmospheric measurements **[1]**, but in recent years it has been started to be applied in other branches of spectroscopy too. Recently, the area of laser-induced breakdown spectroscopy (LIBS) has also discovered the potential of SHS **[2, 3]**. The main appeal of SHS detection in LIBS includes the compactness and robustness of the setup (in view of field applications) and the flexibility to optimize the setup for either high sensitivity or for high resolution, which can be beneficially exploited in applications like stand-off measurements, quantitative analysis with isotope resolution, etc..

In the present work, we have improved and further optimized our initial LIBS-SHS setup described at a previous conference **[4]**. By using optical simulations, we have modelled the light transmission efficiency, instrumental function and imaging properties of the system. We significantly improved and automated the spectral and image data processing sequence. The optimizations carried out resulted in an improved spectral resolution and repeatability, a lower spectral background and the elimination of the central line artifact originating from the Fourier transformation procedure. A detailed characterization of the LIBS spectroscopy performance (e.g. resolution, spectral coverage, tuning range, linearity, etc.), including a comparison with that of a LIBS setup based on a conventional dispersion CCD spectrometer, was also performed.

Keywords: LIBS

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WP-43 Experimental optimization and assessment of the performance of laser-induced breakdown spectroscopy for the quantitative analysis of 20+ trace elements in uranium dioxide

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The physical and chemical properties of nuclear fuel pellets produced by UO_2 are very strict due to the effect on nuclear chain reaction in the reactors. Thus technically suitable, safe, effective and economic operation of a nuclear power plants needs pure UO_2 fuel. However, some elements are added to the UO_2 raw material during the production as reactor poisons (e.g. Gd, Eu) or for any other reasons (e.g. W, Mg) depending on the production technology. For example, the presence of high concentration of boron (or other neutron capturing agents, such as Gd, Eu, Dy, Sm or Cd) can significantly lower the neutron flux flowing through the uranium oxide, which in turn lowers the caloric value of the nuclear fuel. For this reason, the total boron equivalent of these elements cannot exceed 4 ppm. The maximum allowable concentration limits for other elements are usually in the 100-300 ppm range, but their cumulative concentration shall not exceed 1500 ppm. In spite of chemical purification of the UO_2 elemental contamination (impurities), as well as specific elements mentioned above can be useful for origin assessment of nuclear fuel. However, the determination of impurities are challenging because these get concentrated in different regions of a fuel pellet due to production technology (sintering).

Laser induced breakdown spectroscopy (LIBS) is a quick and robust multielemental analytical technique that requires practically no sample preparation and can be employed even from a distance. It is typical limits of detection are in the 1-50 ppm range, therefore one can consider LIBS to be a near ideal candidate for the compositional testing of the trace contaminants in uranium dioxide powders and pellets. Interestingly however, there are only a few articles in the otherwise ample LIBS literature that address the analysis of UO_2 samples and only a couple of attempts have been made to quantify contaminants.

In this study, an Applied Photonics 25+ portable LIBS system was used for experiments. In order to prevent any leak of uranium-containing aerosol generated during the measurement, a closed, pressure-controlled ablation cell was designed and fabricated. Experiments were carried out in argon, helium, air and nitrogen atmospheres, in a range of pressures (100 mbar to 5 bar) in order to optimize the sensitivity and to reduce spectral interferences. Other experimental approaches (e.g. spatial confinement, magnetic confinement, gate delay optimization, multi-pulse plasma generation, etc.) has also been tested in hope for optimizing the detection limits. The maximization of sensitivity, as well as the minimization of spectral interferences caused by matrix components in UO_2 samples was also our motivation in developing a spectral line selection software based on the NIST spectral database.

Analytical figures of merit for this LIBS method were assessed by using certified commercial uranium-oxide standards and in-house prepared pellet samples. The accuracy of the analysis was validated by ICP-MS measurements of the acid-dissolved samples. The goal of the present study was to achieve a quantitative analytical performance that fulfils the requirements described in the ASTM standard specification for 24 trace elements in UO_2 powder **[1]**.

Keywords: LIBS

Acknowledgments

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WP-44 Shaping LIBS into a suitable tool for direct characterization of single nanoparticles: a brave new world

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The combination of optical catapulting, in-air optical trapping and laser-induced breakdown spectroscopy as an effective approach for the analysis of single nanoparticles was first reported in 2014. Since then, this technology, named OC-OT-LIBS, has matured to become an extremely sensitive solution for the direct interrogation of such scarce sample quantities. The actual bottom inspection limit was set in ^{73}Cu attograms, the mass of a single 25 nm Cu particle, leading to an absolute limit of detection (LOD) of ca. 59 ag for this element. Complementary studies of the experimental results have shed light into the mechanisms behind the atomization and subsequent excitation to emissive states of the individual nanoparticles and their efficiency. A clear inverse proportionality between particle mass and excitation efficiency was observed. However, several challenges still lie in the horizon to push OC-OT-LIBS a step higher in the field of nanoinspection. In this communication, a scheme for improving the technique's sampling throughput based on custom 3D-printed skimmer cones is presented. This procedure significantly drops the time required for stable particle trapping, thus allowing analysis to be completed in ca. 3 minutes and significantly reduces the chances of particles other than the trapped one inferring in spectra. Moreover, single multicomponent nanoparticles, namely 9018 nm in diameter $CuFe_2O_4$ (average m = 2.06 fg) and $CuZnFe_2O_4$ (average m = 2.09 fg), are probed in order to demonstrate the simultaneous multielemental detection capabilities of OC-OT-LIBS. Individual LODs are provided as well as excitation efficiency for each metal. Finally, preliminary advances on the application of ultrashort laser pulses for individual nanoparticle LIBS analysis are discussed for the first time with an emphasis on the mechanisms responsible of the particle excitation and how they compare to those acting in ns-OC-OT-LIBS.

Keywords: Nano, LIBS, single nanoparticle analysis, attogram sensitivity, optical trapping, plasma/particle interaction

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WP-45 Advanced analysis of $Li_7La_3Zr_2O_{12}$ (LLZO) using LIBS: determination of the H-content.

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Since current Li-ion batteries suffer from problems caused by the chemical instability of their utilized organic electrolytes, it is of major interest to replace them by more stable inorganic solid ion conductors. Due to their high Li-ion conductivity, cubic $Li_7La_3Zr_2O_{12}$ (LLZO), garnets are among the most promising candidates for future all-solid-state batteries **[1]**. Unfortunately, LLZO shows high reactivity with water leading to H^+/Li^+ exchange in its crystal structure **[2]**. To fully understand this phenomenon as well as to investigate its impact on possible applications of the garnets, information about the exact H uptake is required.

In this work, we present a laser induced breakdown spectroscopy (LIBS) method for the quantitative analysis of H in LLZO garnets. To obtain reliable signal calibration, matrix-matched standards were prepared by pressing mixtures of calcinated LLZO-precursors and $La(OH)_3$ powder into pellets. The developed procedure was used to conduct depth-profiling experiments on various LLZO samples, confirming the presence of significant amounts of H in the garnets.

Keywords: LIBS, hydrogen, depth profiling, Li ion batteries, LLZO

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WP-46 A systematic comparison between millisecond and microsecond dwell time SP-ICP-MS for the selective discrimination of silver nanoparticles from ionic silver as required for biomedical applications

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The incorporation of engineered nanoparticles into a range of industrial and consumer products has increased significantly in recent years. The widespread use of these nanomaterials has led to safety concerns, due to their potential impact on human health and environment. Silver-based nanomaterials are widely used due to their antimicrobial properties. These properties have made them attractive for use in biomedical applications. In this area, information about silver release cannot be limited to the determination of total silver concentration, but information about particulate and dissolved silver is required for a better understanding of the toxicological effects of these nano-devices. The need to deal with Ag-NP in biological media poses major analytical challenges mostly driven by their possible transformation, which potentially occurs during sample storage and preparation **[1]**.

Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been proposed as a powerful tool for the detection, characterization and quantification of samples containing inorganic nanoparticles at ultratrace levels **[2]**. Moreover, this technique allows to differentiate between dissolved and particulate forms of the element in a sample. The feasibility of SP-ICP-MS is compromised by the achievable size detection limits, which are critically affected by the presence of a high background signal. This background signal can be due to different isobaric and matrix/plasma polyatomic interferences, as well as to the presence of dissolved species of the element measured. The latter is well known to hamper the size limits of detection of Ag-NP.

This work presents a systematic comparison of single Ag particle detection using millisecond and microsecond dwell times in the presence of different Ag-NP-to-ionic Ag ratios by SP-ICP-MS. This is achieved in a TMAH-Triton complex matrix, which was proven feasible to preserve nanoparticle stability after Ag-NP quantitative extraction from blood serum. The potential of SP-ICP-MS with microsecond dwell time under optimal conditions was demonstrated for the selective discrimination of Ag-NP from ionic silver (both released from medical devices into human serum) for further determination of Ag-NP number concentration. Remaining challenges of the presented approach and proposed suggestions to further improve the NP size limit of detection will also be discussed.

Keywords: single particle ICP-MS, silver nanoparticles, ionic silver, biomedical applications

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WP-47 Quantification of protein modifications using a multi-elemental ICP-MS/MS generic strategy

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The determination of absolute levels or quantities of a target biomolecule is currently one of the main challenges in Life Sciences, owing to limited availability and accessibility of suitable specific standards. For that matter, inductively coupled mass spectrometry (ICP-MS) can provide absolute quantification of important biomolecules such as proteins without resorting to any species- specific standard prior chromatographic separation. However, HPLC-ICP-MS protein quantification has been limited to the peptide level because of issues regarding chromatographic recovery and resolution for intact protein analysis.

We have recently developed a HPLC-ICP-MS-based quantitative strategy obtaining quantitative recoveries for the analysis of intact proteins, which has enabled the quantification of tens of proteins present in real samples (toxins in snake venoms) with a single generic standard and on-line 34S IDA **[1]**. Moreover, we have further improved such methodology through the optimized and controlled addition of carbon-containing gases to the plasma, leading to the correction of carbon effect in the ionization of heteroatoms. It has proved to be a simpler, more sensitive and cheaper way of addressing quantitative speciation analysis of biomolecules with HPLC-ICP-MS **[2].** Correction of this effect has been demonstrated simultaneously for six of the most abundant heteroatoms (S, P, As, Br, Se, I) present in biomolecules of great relevance in life sciences such as amino acids, proteins, drugs, metabolites, pesticides, etc..

This methodology has also proved high compatibility with molecular MS-platforms, being able to combine HPLC-ESI-MS and LC-ICP-MS information (species identification and heteroatom quantification, respectively) for a better comprehensive quantitative characterization of protein species in a given sample. Moreover, applications of ICP-MS in life science research, and particularly protein analysis has been greatly benefited by the multi-elemental quantitative capabilities of the proposed strategy.

In this regard, it is now possible to simultaneously quantify with great accuracy and precision elements of biological interest such as S, P or Se, just using a single inorganic standard for each of those elements. One of the main proved applications has been the quantitative characterization of protein modifications of great relevance that entail the presence of heteroatoms. Thus, the proposed approach herein turns up as a simple, generic, straightforward and robust alternative for the quantification of post-translational modifications like phosphorylation (P/S), chemical modifications that affect proteins biological activity such as arsenic-binding (As/S), or the characterization of biologically-relevant incorporation or presence of certain heteroatoms in proteins, *e.g.*, selenoproteins (Se/S), or iodinated proteins (I/S).

Keywords: ICP-MS/MS, HPLC, protein analysis, absolute protein quantification, post- translational modifications

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WP-48 Quantification of cancer biomarkers in single cells using metal-tagged antibodies and SC-ICP-MS

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Being breast cancer a major cause of morbidity and mortality in women all over the world, the search for biomarkers that allow its early detection, prognosis and the prediction of drug response is a growing field of research. In this regard, deregulation in iron homeostasis has been linked with breast cancer progression, aggressiveness and recurrence **[1]**. The regulation of iron homeostasis involves a number of proteins, including transferrin and ferritin, which are tightly related to iron uptake and storage, respectively. Particularly, the upregulation of iron importers and the downregulation of iron exporters causes the necessary increase of intraceullular iron that is needed for the fast proliferation and survival of cancer cells. Transferrin receptor (TfR) is a membrane glycoprotein that mediates in the cellular uptake of iron from the plasma protein transferrin (Tf). Due to the higher iron amounts that are needed by cancer cells to ensure their proliferation, a higher expression of membrane TfR is expected to be related to a higher malignancy of breast tumours.

Several methods have been developed for the quantification of transferrin receptors in cell cultures or even tissues. However, being a membrane protein, its determination is not so straight- forward and furthermore, no methods have been shown to quantify transferrin receptors at the single cell level, which can provide valuable information from small cell populations that would be hidden by the vast majority of cells in bulk analysis. Therefore, we have developed a methodology that allows the quantification of transferrin receptors by single cell inductively coupled plasma mass spectrometry (SC-ICP-MS) in combination with metal-labelled antibodies and a dedicated sample introduction system. The results obtained with this approach will be evaluated and compared with those obtained by traditional immunoasays (ELISA) and by a self-developed element-tagged immunoassay that allows TfR quantification by ICP-MS.

Keywords: single cell, ICP-MS, biomarkers, cancer

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WP-49 A higher order method for the determination of total phosphorus in human serum

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Phosphorus is an essential element in the human body and an important clinical biomarker in serum. The importance of phosphorus in the human body manifests itself in the myriad structural and functional roles as an essential element in cellular structure as well as energy metabolisms **[1].** The normal serum phosphorus concentration is 2.5 to 4.5 $g.L^{-1}$ (0.81 to 1.45 $mmol.L^{-1}$) **[2]**. However, the lack of reference method that is traceable to the International System of Units (SI) and matrix-matched certified reference material (CRM) pose a major challenge in the assessment of the accuracy of phosphorus measurements. Moreover, no method for serum phosphorus determination is listed in the Joint Committee for Traceability in Laboratory Medicine (JCTLM) database for reference measurement methods/procedures **[3]**.

A higher order measurement procedure for total phosphorus in human serum by standard addition method using high resolution sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) will be presented. In this method, germanium and gallium are used as internal standards. The accuracy of the measurement was evaluated by comparing the results with the certified values of trace elements in tea leaf powder (NMIJ CRM 7505-a) and trace elements in milk powder (CRM 7512-a), as well as the reference value of electrolytes in frozen human serum (NIST SRM 956d). This method had also been applied in an international inter-laboratory comparison (CCQM-K139 Elements in Human Serum). The results of the comparison demonstrated that the developed method was comparable with methods used by other established national metrology institutes (NMIs) or designated institutes (DIs). The method was then applied in the development of the first human serum reference material certified for phosphorus. This CRM is potentially valuable for clinical laboratories for method validation or as quality control materials which, in turn, will assist in providing more accurate diagnosis for patients.

Keywords: total phosphorus, human serum, standard addition method, international interlaboratory comparison, certified reference material

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WP-50 Conventional immuno-PCR in combination with inductively coupled plasma mass spectrometry for the determination of proteins: human epidermal growth factor receptor 2 (HER2).

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Detecting and quantifying proteins that enable disease diagnosis and prognosis (biomarkers) has been a main issue for clinical research during the last half century. Enzyme-linked immunosorbent assay (ELISA) has been one of the most commonly used technique for this purpose. However, there are other methodologies, such as immuno-polymerase chain reaction (Immuno- PCR) **[1]**, that are also suitable for protein detection and quantification, and sometimes even with higher sensitivity than ELISA. Immuno-PCR is similar to ELISA, which detects an antigen– antibody reaction, but instead of using an enzyme-conjugated antibody, the antibody is labelled with a DNA fragment, which can be amplified by PCR. The amount of PCR products is proportional to the amount of antigen (target protein) that is detected by the antibodies.

In this work, a new Immuno-PCR based method for protein determination has been developed. The new method combines the amplification capacity of conventional PCR with the quantification of the PCR products by inductively coupled plasma mass spectrometry (ICP-MS). This developed methodology has been applied to the accurate determination of the human epidermal growth factor receptor 2 (HER2) protein in biological samples (cell cultures and human serum). HER2 is an important breast cancer biomarker **[2]**, since breast tumours that exhibit elevated levels of HER2 are more aggressive and more likely to recur. Therefore, accurate determination of serum HER2 values is critical to optimizing clinical outcomes in patients with breast cancer.

Keywords: ICP-MS, cancer biomarker, Immuno, PCR, ELISA, HER2

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WP-51 Analysis of chromium and other trace elements in whole blood

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The presence of too high or too low concentrations of elements in blood can be an indication of a deficiency or an intoxication potentially leading to diseases. For this reason, the metallic profile of biological samples such as blood, serum, plasma and urine is routinely analyzed. Here, we present a robust method for obtaining a metallic profile of whole blood with concentrations ranging from ppt to ppm level using alkali dilution for easy and fast sample preparation. The accuracy and robustness of the method was proven by measuring different certified reference materials and whole blood sample spikes. The concentration of all elements was within the range specified over the entire measurement. With the patented BOOST technology, also elements which are typically difficult to measure in whole blood with ICP-MS such asAs, Se, Cr, V were analyzed correctly over 8 hours.

Keywords: whole blood, BOOST technology, chromium

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WP-52 IDMS based quantification methods for metalloproteins as potential biomarkers for Alzheimer's disease

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According to estimates over 6 million people are affected in the European Union by neurodegenerative diseases which pose a big challenge to the health care systems. In an ageing population, the diagnosis and treatment of these diseases are gaining more and more importance. With about 70 % the most common form of dementia is Alzheimer's disease (AD). As the determination of the common biomarkers for AD in routine laboratories often hampers comparability, reliable and traceable quantification methods in AD diagnosis are urgently needed. Furthermore, it might be reasonable to extent the spectrum of biomarkers for AD. Besides the established biomarkers, metalloproteins are under discussion as potential clinical markers. For example, ferritin (FER) levels in cerebrospinal fluid (CSF) are in correlation with brain iron levels which are increased in AD. Further promising candidates for the monitoring of the progress of AD are the Cu-storage protein of the organism, ceruloplasmin (CER), which acts also as ferroxidase, and the Cu and Zn-containing superoxide dismutase (SOD1). A promising quantification method which delivers results traceable to the International System of Units (SI) is the species specific isotope dilution inductively coupled plasma mass spectrometry (SS-ID-ICP-MS). To perform double SS-IDMS, a protein reference as well as a species-specific isotopically labeled protein (spike) is needed. As for the most proteins neither suitable reference material nor isotopically labeled spike material are commercially available, pure native proteins are characterized in-house for the use as reference. Furthermore, ^{65}Cu enriched species- specific protein spikes are prepared for CER and SOD1 in two steps including a demetallation and a remetallation step. As for FER a quantification via the S-content is aimed, recombinantly produced FER enriched in S-34 acts is used as spike.

Keywords: clinical chemistry, Alzheimer's disease, isotope dilution mass spectrometry

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WP-53 Mass spectrometry imaging in clinical pathology: MMP-11 as a breast cancer biomarker

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Pathological processes of breast tumour progression and metastases are associated with matrix metalloproteinase (MMPs), which are a family of structurally related, zinc-dependent endopeptidases, and are implicated with malignant tumour growth. MMP-11 in particular is expressed in many invasive human tumours and high expression levels correlate with poor clinical outcome in breast cancer patients. In this work, mass spectrometry imaging was applied to the investigation of MMP-11 and its role in human breast cancer. Quantitative LA-ICP-MS was applied to map trace element expressions in the heterogeneous environments of cancer tissues. A tryptic on- tissue digestion in combination with MALDI-MSI was also used to target MMP-11 fragments and to investigate co-localisations with Zn integral to MMP-11. Finally, immunohistochemistry assisted LA-ICP-MS was used to target MMP-11 directly. A gold nanoparticle immunoassay was developed to directly locate MMP-11 in breast cancer samples and interrogate MMP-11 for metastasis formation. Mass spectrometry imaging by IHC, LA-ICP-MS and MALDI-MSI provided useful insights for MMP-11 as a versatile biomarker for breast cancer status and diagnosis.

Keywords: laser ablation, immunoassay, bioimaging, biomarkers

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WP-54 High resolution imaging of explant cultures to predict cisplatin resistance in anticancer therapy

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Preclinical models of patient response are urgently required in order to improve our understanding of the mechanisms of drug action in cancer treatment. Such models can predict the chemotherapeutic benefits of emerging therapies, as well as facilitating more targeted use of existing drugs, to provide improved clinical outcomes. Karekla *et al*. recently reported the development a preclinical 'explant' model of non-small cell lung cancer **[1]**. Patient derived lung tumour biopsies were grown on *in vitro* and dosed with cisplatin. Histological staining was subsequently used to classify the tumours as either cisplatin sensitive or cisplatin resistant at each of the doses studied (1, 10 and 50 mol.L^{-1}).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) offers a high resolution approach to image metallodrugs in tissue samples. The technique has previously been used to evaluate the penetration of platinum containing drugs in multicellular spheroid models of tumours **[2]**. Recent developments in the core technology have provided dramatic improvements in the throughput, spatial resolution and absolute sensitivity of LA-ICP-MS systems, therefore improving the applicability of the technique to the clinical setting **[3]**. Here we report the application of a low-dispersion laser ablation system, the NWR image, to image platinum in explant tissue. We correlate the distribution of platinum with histological images and patient outcomes and offer insights on the relationship between cisplatin dose, tumour penetration and drug resistance.

Keywords: bioimaging, laser ablation, cisplatin, cancer, explants

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WP-55 Analysis of trace impurities in sunflower oil by HR-ICP-OES

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The PlasmaQuant® PQ 9000 High Resolution Array ICP-OES equipped with an temperature cooled spray chamber was used for the analysis of As, Cd, Hg, Pb, Ca, Mg and P in sunflower oil. For such materials, unspecific spectral emission lines originating from organic matrix often hamper the analysis of trace elements like Phosphorous due to spectral interferences. Given the high spectral resolution of PlasmaQuant® PQ 9000 of less than 3 pm in case of Phosphorous and Arsenic such undesired spectral interference can be removed. Hence, the quality of the baseline fit, precision and method robustness as well as the limits of detection improve significantly.

Keywords: sunflower oil, HR-ICP-OES, robust plasma

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WP-56 Multi-element determination in populations of single cells by ICP-MS

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Recent advances in elemental analysis of single cells has delivered ICP-MS into widespread roles in the field of biological research **[1-3]**. Using single cell analysis, there have been many efforts that try to quantify the concentration of drug elements in cancer cells and to assess the effect of toxic elements **[4]** and nano particles on the environment. Single cell analysis using ICP-MS is performed by suspending cells in solution to separate them, cells are vaporized and ionized using an Ar plasma and ion cluster is measured as a signal pulse at the ICP-MS detector lasting 0.4-0.6 msec. Therefore, single cell analysis allows cells to be injected individually, enabling us to understand the detailed elemental profiles of whole cell clusters. Previously, we showed our sample induction system could determine the µm size cells well. Now, our new sample introduction system comprising a low flow nebulizer and a total consumption spray chamber greatly improves the transmission efficiency of cells and has enabled us to quantify the concentrations of major elements such as Mg, P, S, K, Ca, Fe, and Zn at ag.cell^{-1} level in bakery yeast cells (*Saccharomyces cerevisiae*). In terms of our software, it can monitor 16 elements within the same batch, and also it calculates the number of cells in the sample and the analyte concentrations in the cells automatically. In this presentation, we will show the fundamental results based on the new hardware and software development for the single cell analysis.

Keywords: ICP-MS, single cell analysis, metallomics, microorganism

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WP-57 New strategy for sensitive detection of circulating tumoral cells (CTCs) for breast cancer diagnostic

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Circulating tumor cells (CTCs) are highly mobile cells that reach the bloodstream from a primary tumor. When a tumor cell penetrates through the basal lamina, arriving to the bloodstream, it becomes a potential distant metastasis risk. The extravasation can take place due to a tropic factor or an external pressure coming from the primary tumor. In the first case, tumor cells acquire their mobility due to a process called "Epithelial Mesenchymal Transition" (EMT). During this process, cells change their protein expression pattern, decreasing epithelial markers which provide adhesion and polarity to the cells. In the case of epithelial breast circulating tumor cells, proteins such as Epithelial Cell Adhesion Molecule (EpCAM) or Cytokeratins (CKs) 7, 8, 18 and 19 are increased. Consequently, CTCs can be differentiated from healthy cells **[1]**.

The detection of CTCs in blood can be used as a diagnostic method in liquid biopsy, facilitating an early diagnosis. The main difficulty of such procedure lies on the low concentration of CTCs in the bloodstream. Usually, there are between 1 and 100 CTCs for each 5x109 blood cells. Thus, it is important to preconcentrate CTCs before their detection **[2]**.

Nowadays, there are a large number of methods for the determination of CTCs based on their different properties, including physical properties (size, density, charge…) and biological properties (surface protein expression). Due to their high specificity, immunocapture-based methods tend to be the most used for preconcentration and/or separation of CTCs from the surrounding normal blood cell. Once CTCs are isolated, the detection usually is carried out by fluorescence microscopy or flow cytometry, thanks to the use of fluorescent marks directed against CTCs. However, the number of these marks that can be employed simultaneously is limited to the number of fluorescence spectra that can coexist without overlapping. Consequently, not all CTCs families can be detected at the same time in the sample. By contrast, ICP-MS allows a simultaneous multi- elemental marks detection **[3]**.

The aim of this work is the development of a new strategy for CTCs preconcentration/separation and their subsequent sensitive detection by ICP-MS. Our first approach is the preconcentration/separation of CTCs using micromagnetic beads conjugated to anti-EpCAM. The magnetically separated cells (CTCs) are specifically targeted with anti-CK19 bioconjugated to metallic nanoparticles for its specific and sensitive detection by ICP-MS.

Keywords: breast cancer, diagnostic, circulating tumor cells, ICP-MS, immuno-capture

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WP-58 Optimization of protein quantification via isotope dilution ICP-MS of a standard reference protein

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Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful method for the matrix-independent quantitative analysis of target elements. Developed for the use in inorganic trace analysis, ICP-MS is nowadays emerging as a valuable tool for bioanalytical questions. Especially, the use of ICP-MS for quantitative proteomics by measuring heteroatoms is highly promising, considering that established quantification methods like organic mass spectrometry depend on the existence of matched protein and peptide standards or labelling of the target protein. In this work, we applied isotope dilution analysis (IDA) using ICP-MS to quantify proteins of known stoichiometry via their sulfur content. Sulfur is present in two amino acids, cysteine and methionine, and hence exists in nearly all proteins. A standard reference material bovine serum albumin (BSA) from NIST was quantified using sulfur IDA to optimize sample preparation and method parameters. We compared different sample preparation methods regarding their quantitative recovery of sulfur and employed simple strategies for the detection of low molecular sulfur species to validate the results. We report recoveries for the protein content measured by IDMS and evaluated the uncertainties. The herein developed method can be applied for the reliable and traceable quantification of proteins, especially pure protein standards, but will also be used for the quantification of other proteins in the future.

Keywords: isotope dilution, sulfur, protein, quantification

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WP-59 Platinum nanoclusters as metal labels to determine specific proteins in biological samples by bimodal detection (LA-ICP-MS and fluorescence)

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Recent advances have enabled facile synthesis of fluorescent metal nanoclusters (NCs), establishing them as a new class of ultra-small and biocompatible labels for biological applications. Although great progress has been achieved, further advances in the development of fluorescent metal NCs are required, such as in case of platinum nanoclusters (Pt-NCs). A methodology based on the combination of antibodies and Pt-NCs to amplify the signal of specific proteins in biological samples is described in this work.

Platinum is a noble, non-toxic, and biocompatible metal and Pt-NCs (with sizes below 2 nm) show a characteristic fluorescence peak **[1]**. On the other hand, it offers the possibility of bimodal detection through fluorescence and elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS). Therefore, the fast and cheaper fluorescence measurements will allow rapid optimization procedures, whereas the ICP-MS allows signal amplification thanks to the high number of Pt atoms per NC as well as absolute quantification capabilities.

First of all, the synthesis of Pt-NCs was developed to obtain highly stable water soluble nanostructures with diameters below 2 nm composed of more than one hundred atoms (120 atoms of Pt). This small size allows the bioconjugation to specific antibodies with their functionality unaltered, even using high molar ratio (Ab:Pt-NCs 1:20). Also, the characteristic fluorescence of this type of materials shows an intense and highly stable emission peak (620 nm). The Pt-NCs stability has been evaluated during several months (storing under different conditions and solvents), offering promising results. Secondly, quantitative immunoassay optimizations have been carried out to achieve the determination of specific proteins (biomarkers) in biological samples using Pt-NCs as fluorescent (measuring bioconjugated emission) and metal labels (measuring Pt by ICP-MS). The applicability of the sensitive competitive immunoassay was assessed by successful analysis of the biomarkers (proteins) in human serum and results were compared with those from a commercial kit. Moreover, laser ablation ICP-MS was used for protein imaging in ocular tissue sections.

In our experiments, we have used a Pt standard with natural isotopic composition. However, the possibility of developing multiplexing assays using different isotopically-enriched Pt spikes is now our goal. Pt-NCs can be synthesized using different isotopically-enriched spikes and then bioconjugate each with different proteins that can be measured simultaneously.

Keywords: platinum nanoclusters, proteins, bimodal detection, fluorescence, ICP-MS

Acknowledgements

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WP-60 Modified method of single cell analysis by quadrupole ICP-MS

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Single cell-ICP-MS or single particle-ICP-MS is an emerging technique for the analysis of nanoparticles or cells **[1,2].** It is well known that conventional ICP-MS with a quadrupole mass analyzer has limitation in such analysis, due to the one mass measurement at a time. This contrasts with the simultaneous multi-elemental analysis performed by ICP-TOF-MS, in which a broad range of isotopes can be measured.

In this project, a modified method of single cell analysis using ICP-Q-MS was attempted. Two masses were monitored (2-mass mode) during the analysis in comparison to that of single mass in the conventional approach in single particle-ICP-MS analysis. Information such as particle size, number of particles and the size distribution profile obtained by the two modes were compared.

The proposed method was proved successful in mixtures of Ag-NP and Au-NP with different particle size. The sizes determined by the two analysis modes were in a good agreement with each other. The percentage difference of the evaluated parameters of the two modes are within the acceptable range, demonstrating the potential of 2-mass mode in comparing two elements in cells or nanoparticles. Furthermore, the developed method was used in the analysis of single-cell algae treated with nanoparticles, to study the nanoparticle uptake of the cells after exposure. ICP-TOF- MS was also employed to supplement the information obtained by the ICP-Q-MS. Although the amount of information retrieved is not comparable to that by ICP-TOF-MS, the success of the current approach can extend the capability of ICP-Q-MS for multi-elemental detection in single cell level, offering useful information for single particle/cell analysis.

Keywords: single cell, ICP-MS, nanoparticles, inductively coupled plasma, quadrupole mass spectrometry, inductively coupled plasma time of flight mass spectrometry

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WP-61 Investigating hereditary hemochromatosis by means of LA-ICP-MS/MS

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Hereditary hemochromatosis is an autosomal recessive inherited disorder of the iron metabolism characterized by over-absorption of iron in the intestine and excess iron storage in organs. The systemic iron homeostasis is mainly regulated by the hormone hepcidin. If the induction of hepcidin is hindered, iron is accumulated unregulated in various organs, especially in the liver and pancreas. Due to the redox activity of iron, the accumulation leads to a wide variety of often non-specific symptoms. Some of the observed symptoms are liver cirrhosis, an increased risk of hepatocellular carcinoma, diabetes, skin hyperpigmentation or arthritis. Since the bone morphogenetic protein type I receptors ALK2 and ALK3 are essential for the hepcidin expression, hepatocyte-specific *Alk2* or *Alk3* deficient mice, in which one or both of the receptors are knocked out, present with severe iron overload. Thus, they can be used as an animal model for hereditary hemochromatosis.

The mechanism of the iron accumulation is not fully understood by now. Therefore, a further investigation of the iron distribution in the affected organs is required to gain more information about the pathophysiological development of the iron overload. The established method to determine the iron distribution in tissue is Prussian blue staining, but with this approach, only qualitative data can be obtained. Here, laser ablation inductively coupled plasma triple quadrupole mass spectrometry (LA-ICP-MS/MS) was used to quantify the iron distribution in mouse tissue. Quantification of iron was achieved by the use of matrix matched gelatin standards spiked with different amounts of iron sulfate.

Due to many polyatomic interferences affecting the most abundant iron isotope ^{56}Fe, a triple quadrupole ICP-MS with oxygen as reaction gas was used. With this instrumental setup, the mass shift of ^{56}Fe to $^{56}Fe^{16}O$ is monitored to obtain significantly better limits of detection. Moreover, the phosphorous and sulfur distributions could be analyzed in the triple quadrupole mode. To differentiate between the periportal and centrilobular liver regions, a small laser spot size of 4 µm was used. For this high spatial resolution analysis, the low limits of detection are necessary. With the developed method, the iron distribution and concentration in liver and pancreas samples of different knock-out and wild type animals were successfully analyzed.

Keywords: bioimaging, laser ablation, triple quadrupole ICP-MS, iron, hemochromatosis

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WP-62 Advances in triple quadrupole ICP-MS for clinical research analysis.

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Since its introduction in the early 1980's ICP-MS has become an established analytical technology in a wide range of areas including clinical research. The technique is well known to be affected by polyatomic interferences derived from combinations of the sample components and the plasma gas, as well as isobaric interferences from the overlap of isotopes of different elements that have the same mass. Development of collision cell technology for interference removal has provided a major improvement, but even this innovation does not fully remove every polyatomic interference or solve the problem of isobaric interferences.

With the advent of triple quadrupole ICP-MS, a new level of interference removal has been achieved. The implementation of an additional quadrupole before the collision cell of the instrument allows pre-filtering of the ion beam to selectively transmit only the masses of interest, which alleviates the problem of unwanted side interference production in the cell through collisions between other masses in the sample and the cell gas. This pre-filtering capability also allows selective chemical reactions to be conducted in the cell to enhance polyatomic interference removal and, in many cases, solve the problem of isobaric overlap.

In this presentation, the latest advances in triple quadrupole ICP-MS technology and how these benefit clinical research analysis will be described. Use of this technique to improve the accuracy of Se analysis in research specimens containing Gd to simulate the presence of Gd based MRI contrast enhancing agents will be presented. In addition, the capability of triple quadrupole ICP-MS to enhance the measurement of elements such as P and S for clinical research studies will be described.

Keywords: clinical research, triple quadrupole ICP-MS

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WP-63 An integrated LC-ICP-MS and LC-ESI-MS approach for the characterization of purified selenoprotein P

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Selenium is an essential trace element known for its antioxidant activities. In mammals, selenium deficiency has been associated with muscular, neurological and immune disorders, and also with an increase in cancer incidence and mortality **[1]**. The vital role of selenium has been widely recognized by selenium supplementation of the diet **[2]**. The physiological role of selenium is principally awarded to its co-translational incorporation into selenoproteins as selenocysteine (SeCys), referred to as the 21st amino acid. Twenty-five selenoproteins have been identified and constitute the human selenoproteome **[3]**. It has been recognized that most biological functions of selenium (Se) are mediated by specific proteins such as the selenoprotein P (SelP), which is the major selenoprotein in plasma (up to 10 SeCys in its sequence) responsible for transport and distribution of Se. Furthermore, SelP has also been associated with neurodegenerative diseases such as Alzheimer's and Type 2 diabetes **[4]**.

Due to its low abundance and the complexity of its biological samples, the full characterization of SelP, its multiple isoforms and post-translational modifications (*e.g.* glycosylations, Se-S bridges) is critically dependent on the availability of protein pre-concentration techniques and adequate analytical methodology.

Here, we present a method for the purification of SelP from human blood using affinity chromatography and its characterization by an integrated HPLC-ICP-MS and HPLC-ESI-MS approach. Two chromatographic steps, immobilized cobalt and heparin affinity chromatography, allow the purification of SelP with a selectivity exceeding 1000. Moreover, the sensitivity and complementarity of ICP- and ESI-MS allow for the first time all selenocysteine containing peptides in SelP to be characterized and some glycosylations sites elucidated. Our results contribute to the metrology of SelP based on the use of selenopeptides **[5]**.

Keywords: selenium, selenoproteins, HPLC-ICP-MS, HPLC-ESI-MS, health

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WP-64 Direct analysis of trace elements in beer and wort by ICP-OES

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Even though most metal ions are only present in traces in wort and beer, but they still play a considerable role for the brewing process and for the finished product as they influence the mash, wort and beer pH. The metal ions are also important yeast nutrients that affect foam stability and are involved in flavor deterioration reactions. Especially, transition metal ions like iron, copper and manganese can constitute in beer staling by acceleration of oxidative processes, as they can activate oxygen by electron transfer and catalyze the Fenton- / Haber-Weiss reactions system resulting in formation of reactive oxygen species (ROS). Because of the low concentration levels especially found for Fe and Cu, it is desirable to avoid dilution of the samples before analyses via ICP-OES. The analysis of beer is complicated by the presence of alcohol, dissolved solids and carbonation. The alcohol content requires matrix matching the standards to the samples containing ethanol. Also, the sample introduction system must be optimized for the volatile, organic ethanol component of the matrix. Due to high levels of dissolved solids, the nebulizer and injector must be capable of handling the samples without clogging. The carbonation in the beer samples must be removed to prevent out-gassing during the nebulization process and to eliminate poor reproducibility.

Keywords: metal analysis, ICP-OES, wort, beer

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WP-65 Challenges in bio-monitoring – Total and single particle analysis

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For many years, the ICP-MS spectrometry is a tool of choice for the trace analysis of elements like Pb, As, Hg, and Cu in body fluids such as urine, blood, serum and saliva as well as in tissues. Single elements or panels of toxic or nutritional elements are run in these matrices providing doctors with comprehensive views on patient conditions.

The goal of this presentation is to demonstrate the research capability of the current ICP-MS technology for trace element analysis in body fluids. A winning combination of reaction/collision spectral interference removal allows for the accurate determination of the low levels of analytes of interest.

Recently, due to the popularity of implants, elements like Ti and Co were added to the common list of tested analytes. They are non toxic but can give medical providers information on an implant degradation. It will be shown that the current ICP-MS technology can assess implants degradation level not only by measuring the total Ti content but also by using the single particle technique. The single particle ICP-MS offers a better understanding of the degradation process of implants and an improved detection limits allowing earlier diagnosis.

In summary, the ICP-MS, in combination with an optimized sample introduction system, is a perfect technique for the analysis of diverse types of biological matrices including urine, serum and blood for total concentration and single particle analysis. One simple sample preparation technique, the appropriate diluent and panels or individual analytes can be measured quickly and precisely. The results in reference materials will be shown and discussed.

Keywords: bio-monitoring, titanium, single particle analysis, serum

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WP-66 Size exclusion chromatography ICP-MS for trace level detection of gadolinium species accumulated in rat brain one month after single intravenous injection with gadolinium contrast agents

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Since 2015, multiple retrospective clinical studies have shown long-term presence of gadolinium in the patients' bodies, including the brain after repeated administrations of gadolinium- based contrast agents (GBCAs) **[1]**. This phenomenon is particularly pronounced for linear GBCAs compared with macrocyclic ones and was reproduced and studied on the preclinical model **[2]**.

Until now, no clinical consequences of Gd presence in the brain have been demonstrated. However, it is well known that non-chelated gadolinium Gd^{3+} is toxic at the dose for imaging and administration of linear GBCAs to the patients with renal insufficiency may provoke nephrogenic systemic fibrosis **[3]**. In order to assure safe clinical use of GBCAs, it is crucial to study its potential toxicological impact. While the total concentrations of Gd in different brain structures have been investigated, the speciation of gadolinium in brain is poorly understood. In other words, it remains uncertain if gadolinium retained in the brain is still in its chelated form (GBCA), was metabolized or was dissociated from its ligand and interacted with some endogenous molecules. Furthermore, although some molecular Gd species in the cerebellum after repeated injections with linear GBCAs at clinical doses have been detected **[4, 5]**, those of single clinical dose injection have not yet been investigated.

The aim of this work is to study gadolinium species in the cerebellum after single injection of GBCA at clinical dose (0.6mmol.kg^{-1}). For that purpose, 4 groups of rats (total of 40 rats, N=10/group) were injected with macrocyclic GBCA (gadoterate meglumine), two linear GBCAs (gadobenate dimeglumine and gadodiamide) and with saline solution (control group). The extracted Gd species were separated by size exclusion chromatography and detected by ICP-MS. In order to control global contamination, the SEC-ICP-MS blinded analysis was performed by alternating each GBCA sample with a blank (saline group). Thus, the procedure used for the analysis of a large number of complex samples containing trace level of Gd proved to be robust and the bias of Gd speciation study was reduced to minimum.

Keywords: gadolinium based contrast agent, gadolinium speciation, size exclusion chromatography, ICP-MS

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WP-67 Study of the use of biocompatible nanostructures to improve cisplatin performance in cell models: ferritin as nanocage

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Cisplatin (CDDP) is a widely used antitumor drug that reacts with the DNA generating the so-called DNA adducts. These adducts stop the DNA replication and the RNA transcription taking the cell into apoptosis. However, there are several problems associated with the use of this drug including undesirable side-effects (such as nephrotoxicity) and the resistance that the cells acquire in some cases **[1]**.

To avoid these undesirable problems and to improve the cisplatin treatment, cisplatin can be encapsulated in biocompatible nanostructures. One of these nanostructures can be ferritin. Ferritin is the main iron storage protein in the body. It consists of 24 subunits that form a spherical structure, with an internal diameter between 8 and 12 nm. Within this protein, iron is accumulated in its nanoparticulated form (ferrihydrite). The different subunits can be easily dissociated and refolded in function of the pH. Taking advantage of this possibility, CDDP can be encapsulated in this "nanocage" **[2]** with the aim of improving the drug uptake in the cancer cells and minimizing undesirable side-effects.

The objective of this work was the characterization of the cisplatin encapsulated inside the ferritin cavity. The uptake, DNA binding and viability between encapsulated and free CDDP (not encapsulated) was studied in different cell models using different ICP-MS strategies.

Keywords: ICP-MS, cisplatin, nanocage

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WP-68 A microwave-digestion approach for determination of osmium in chemical drug to meet the requirement of USP< 232> /< 233>

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USP<232>/<233> has become official since January 1st, 2018 and the final version completely aligned with ICH-Q3D, including impurities test of 24 elements. Elemental impurities include catalysts and environmental contaminants that may be present in drug substances, excipients or drug products. When elemental impurities are known to be present, have been added, or have the potential source, the specific levels should be considered according to USP<232>/<233>. ICP-MS is the most widely used atomic spectrometry technique for the measurement of trace elements. Chemical drugs that could not be dissolved in deionized water, nitric acid, or organic solvent, should be decomposed with the microwave digestion method. Analysis of trace level osmium (Os) in chemical drug samples is extremely tough, due to the volatility of OsO_4 during microwave digestion. Typically, the spike recovery of osmium ranges from 30-50%, using nitric acid microwave-digestion system, which seems very difficult to meet the requirements of 70-150%. Here, we show the effect of sample preparation on the measurement of osmium in chemical drug products by ICP-MS. With mixed reductive chemicals, the spike recovery of osmium could be achieved in the range of 90-110%. Usually, hydrochloric acid is used for stabilizing mercury in a closed digestion system. To prevent the formation of osmium oxide, a somewhat large amount of HCl is added to keep osmium stable in the digestion solution. Meanwhile, in this work, we compared high-pressure and low-pressure microwave digestion systems for sample preparation. The method of high-pressure digestion system, coupled with mixed reductive chemicals, could achieve great recovery for osmium analysis, according to USP.

Keywords: osmium, microwave digestion, USP<232>/<233>

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WP-69 Arsenic speciation in human urine after ingestion of husked rice

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Food is one of the main sources of arsenic (As) intake in populations from non-endemic areas. One of the main foods is rice. When compared to other cereals such as rye and barley, rice has on average a 10-fold higher concentration of As **[1]**. Toxicity and carcinogenicity are species dependent. Inorganic species are about 100 more toxic than organic species. Inorganic As in the human organism is methylated and excreted by urine mainly in the form of dimethylarsine (DMA). There is currently no safe intake. Levels between 0.3 and 8 $g.kg^{-1}$per body weight per day increase the risk of lung, skin and bladder cancer. Thus, the speciation of biological samples such as urine is of fundamental importance to evaluate the real risk of ingestion of As through food. A pilot experiment was conducted for 6 days with two participants, a woman (volunteer A) and a man (volunteer B). In the 1st, 2nd, 5th and 6th days, volunteers consumed water and all kinds of food except rice (and derivatives), seafood, fish and derivatives of Asian food. In the 3rd and 4th daysthe feeding was restricted only to husked rice and water. From the 1st to 6th days, the urine and food consumed by volunteers were collected. Then, the total As was determined for food and urine by ICP-MS. The As-species were determined by HPLC-ICP-MS. The total As in food from the 1st to 2nd days and 5th to 6th days varied between < LOD (0.002 $g.kg^{-1}$) to 242.85.65 $g.kg^{-1}$ and water (ingested from 1st to 6th day) was < 10 $g.L^{-1}$ (as recommended by the World Health Organization) respectively. The total As in husked rice (consumed in the 3rd and 4th days) was 240.485.2 $g.kg^{-1}$ (74% inorganic As and 26% organic As). Regarding the mean concentrations of DMA / inorganic As in urine (creatinine-corrected) from the 1st to the 6th day, we found 3.48/2.98, 4.10/4.67, 9.37/3.28, 13.0/2.38, 8.84/2.05 and 6.63/3.13 g g-1 for individual A and 7.83/8.22, 6.25/5.41, 9.94/2.79, 14.03/2.68, 10.47/1.74 and 8.73/2.31 $g.g^{-1}$ for individual B. In the present study, when comparing the mean rates of daily methylation among volunteers, the female volunteer presents a variation between 1.45 and 2.09 times greater in relation to the male volunteer, corroborating thus with the literature **[2]**, in which the methylation of As is more efficient in relation to women when compared to man. It is worthy of investigation to mention that the methylation of inorganic As processes produce oxidative stress which is related to the toxicity and carcinogenicity. These findings are important because they enable a better understanding of the routes of exposure to As through rice intake and its metabolism/elimination for evaluation of risk assessment.

Keywords: arsenic, rice, urine, methylation, ICP-MS, HPLC-ICP-MS

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WP-70 Leaching experiment followed by trace element analysis in fermentation media

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During fermentation, unexpectedly, target molecule quantities and qualities vary despite constant production conditions. One assumption is, that this is due to the concentration of certain trace elements. Therefore, we have carried out a test series where we have monitored the concentration of these trace elements during the fermentation process. Here we describe a leaching experiment, intended to clarify at what working steps concentration changes occur.

Keywords: fermentation, leaching

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WP-71 Mercury determination in dried blood spots

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One of the main trends changing the way in which sampling and analysis of biological fluids is carried out is the formation of the so-called dried matrix spots. If we focus on blood analysis, use of dried blood spots (DBS) is becoming increasingly popular in this clinical context.1

Advantages of using such approach include the possibility for the patients to prepare their own samples, the ease of transportation and preservation, the potential to use them for screening populations in isolated or underdeveloped areas, in addition to the most typical application of controlling newborns.

Recently developed approaches (such as the use of volumetric absorptive microsampling) have even helped to solve some traditional problems such as the hematocrit effect and the unknown volume, as these devices are supposed to sample a constant and known amount of sample regardless of the blood characteristics.

This work evaluates the use of 20 μL VAMS for the determination of Hg in blood samples, using different analytical approaches, such as inductively coupled plasma mass spectrometry after fast sample extraction, or direct analysis via a so-called Hg analyzer. Advantages of both techniques and possibilities for their ultimately coupling will be discussed.

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Keywords: dried blood spots, mercury, blood analysis

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WP-72 A feasible approach for determining bromine and iodine in human hair using interference-free plasma based-technique

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0.24 Human hair analysis is useful when investigating the mineral status of human organisms, as it provides information on diet, environmental exposure, health problems, use of medicines or supplement intake [1]. Nowadays, there is an increasing interest in the determination of bromine and iodine in biological samples, since they play important physiological functions and, in inappropriate concentration they can cause several adverse effects [1-3]. However, the challenge begins with the choice of the analytical tool to be used because only a few techniques provide accurate results for Br and I in biological samples [1-3]. In addition, there are few studies that report the determination of Br and I in human hair with suitable precision and accuracy [2,3]. Instrumental neutron activation analysis (INAA) is a technique commonly used for this goal; however, its application in routine analysis is hampered in view of the nuclear reactor required as source of neutrons, and its relatively low sample throughput [1]. X-ray fluorescence (XRF) and laser ablation- inductively coupled plasma mass spectrometry (LA-ICP-MS) have also been used to determine Br and I in biological matrices [1]. Although these techniques avoid exhaustive sample preparation steps, have multielemental capability and do not require the use of a nuclear reactor, problems related to the matrix effects, calibration step and the lack of sample homogeneity may limit their application in routine analysis. In contrast, inductively coupled plasma mass spectrometry (ICP- MS) using conventional nebulization is a powerful tool for Br and I determination [2,3]. It presents important characteristics for routine analysis, such as suitable selectivity, sensitivity and high sample throughput; however, a suitable sample preparation method is essential for the successful of the analysis. Spectral and non-spectral interferences, such as the formation of polyatomic species, memory effects, physical troubles and signal intensity modifications may occur, if sample preparation method is not suitable, and impair on the determination of Br and I by ICP-MS [2,3]. Thus, an effective sample preparation method for Br and I determination in human hair using interference-free ICP-MS was developed. Human hair was digested based on combustion reaction to obtain compatible solutions with ICP-MS analysis. Using microwave-induced combustion (MIC), masses of human hair ranging from 50 to 300 mg were efficiently digested. A diluted solution (100 mmol L-1 NH_4OH) was used for the absorption of both analytes, which was fully compatible with ICP-MS analysis. Using these conditions low limits of detection (LOD of 0.01 μg g-1 for Br and 0.004 μg g-1 for I) were obtained. Recovery tests at two levels (50% and 100%) using a standard solution and using a mixture of the sample with certified reference materials (CRMs) were carried out and good recoveries between 94% and 102% were obtained. Accuracy was evaluated by the analysis of a CRM of human hair, and the Br and I concentrations obtained by the proposed method did not differ from the certified values. Repeatability (RSDs ≤ 4%) and reproducibility (RSDs ≤ 7%) of the results using proposed method were always suitable. Microwave-assisted extraction using alkaline solutions and microwave-assisted wet digestion using concentrated nitric acid were also evaluated, but they were not considered suitable in view of the high carbon content or high acidity in final solutions, which caused several interferences during ICP-MS analysis. Moreover, results for I were not quantitative when microwave-assisted wet digestion was used for sample preparation, which is probably related to the I losses in acidic medium. On the other hand, the digests obtained using the MIC method were fully compatible with ICP-MS and the interferences currently found using conventional digestion methods were completely eliminated. Ultra-trace concentrations of Br and I were determined in human hair (from 0,24 μg g-1 to 4.17 μg g-1 for Br and from 0.61 to 10.1 μg g-1 for I), demonstrating that the proposed method is a suitable strategy and it presents several advantages compared to the others reported in the literature.

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Keywords: human hair analysis, Sample preparation, Halogens determination, Microwave, induced combustion, Inductively coupled plasma mass spectrometry.

WP-73 Ultra trace U/Th dating of archaeological biominerals applying fsLA-HR-ICPMS

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U-series dating is a well-established dating method covering periods ranging 10 ky to 500 ky. This method is based on the disequilibrium of uranium and his daughters in natural radioactive decay chains. It is particularly useful for dating calcareous materials, and can be applied in many fields, such as geology or archaeology.
Nevertheless, some limitations make the use of the U/Th geochronometer challenging : 1) archeological samples might be affected by late uranium and thorium input (open system) 2) This biominerals contain ultralow U and Th concentration in the preserved areas.
Here, we present a new method to overcome these limitations, taking advantages of the coupling of a HR-ICP-MS with a high repetition rate UV femtosecond laser-ablation. This new approach of U- series dating permits direct measurement of U and Th isotopes. It gives access to the distribution of these elements at ultralow concentration (within few ppq to few ppb), using very small quantities of material. Here is an application of this new protocol to ancient engraved ostrich eggshells from South Africa, samples of one of the first human artistic behaviour.

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PLTH-1 A paradigm change in isotopic measurements by mass spectrometry: isotope abundances, molar fractions and linear regression calculations

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Traditional research in isotopic measurements, both for natural variations and for tracer work, focused on the accurate and precise measurement of isotope ratios. Isotope dilution mass spectrometry (IDMS) equations developed over the years employed isotope ratios in the calculations. On the other hand, isotopic studies focused on natural variations also made use of primary isotope ratio measurements. In this talk, I would like to convince you that much more information can be obtained when the original data is in the form of isotope abundances or raw isotopic signals rather than in the form of isotope ratios, both for the study of natural variations and for tracer work (IDMS, speciation, metabolism studies, traceability, etc.).

The first advantage of linear regression calculations is the internal correction of mass bias and spectral interferences on the measured isotopes. The characterisation of isotopically enriched tracers and the IDMS determination of selenium in biological materials will be used to illustrate these advantages. A second advantage is the simplification of the calculations when several enriched isotopes are used in metabolism, speciation and traceability studies. The study of selenium metabolism, the speciation of mercury and chromium and the transgenerational labelling of fish will be used as examples of those measurements. The study of natural variations in isotopic systems benefits also from linear regression calculations, particularly when transient signals are measured in the multicollector instrument. Examples of these procedures are the laser ablation measurement of Sr isotope ratios for food traceability and Pb isotope ratios for dating purposes. The coupling of gas chromatography and liquid chromatography to the multicollector instrument will be also illustrated. Finally, these alternative procedures can be advantageously implemented in molecular mass spectrometry measurements. Examples are the purity assessment of molecular clusters, the application of minimal labelling in organic and biochemical IDMS, the use of multiple tracers ($^{13}C_1$ and $^{13}C_2$) for the correction of interconversion reactions, the application of ^{13}C metabolic flux analysis, the calculation of the isotope enrichment of labelled molecules and the linearization of mass isotopomer distribution analysis (MIDA) calculations.

Keywords: isotopic measurements, linear regression

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KTH-1 Joint forces of ICP-MS-based techniques for effective examination of the intracellular processing of gold nanoparticles

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There is an increasing demand for advanced nanoscale therapeutics and among these, gold nanoparticles (Au-NPs) proved to afford increased therapeutic efficacy and effective drug delivery. The amount and form in which Au-NPs are taken-up by cells, the speciation of internalized particles, the routes by which they are translocated inside the cell and interacting with subcellular structures can be essential for future approval as anticancer therapeutics. After intravenous administration, the Au-NPs encounter the physiological environment rich of various biomolecules (mainly proteins) that tend to adsorb onto the nanomaterial surface **[1,2]**. The native protein corona formed in this manner governs the biological behavior of Au-NPs. Therefore, it is acute need for developing novel and more efficient techniques to study nanoparticle–cell interactions, the first step of which being testing the formation of the human serum protein–Au-NPs conjugates.

In this regard, the first part of the work was application of direct ICP-MS technique for quantitative evaluation of uptake to cancer cells and distribution inside them the Au-NP-serum protein conjugates. Specifically, a significant impact of the protein corona and particle size on the internalization and location of nanogold in cells was confirmed.

Secondly, the form/size in which Au-NPs are accumulated inside the cancer cell was explored by single particle ICP-MS, thus confirming that the intracellular state of the gold remains mainly as nanoparticles.

Thirdly, the hyphenated ICP-MS techniques were used for the characterization of taken-up AuNP forms in the cytosol of cancer cells. The resolution potential of two separation techniques, coupled to an ICP-MS detector – high performance liquid chromatography and capillary electrophoresis, was tested. The latter technique was qualified to perform the final tests proving: (i) the formation of new AuNP-containing species; (ii) the dynamic character of speciation changes during incubation of the AuNP-serum conjugates with cancer cells; (iii) the significant influence of nanomaterial size on the rate of the observed changes.

Keywords: gold nanoparticles, cancer cells, in vitro, capillary electrophoresis, single particle ICP-MS, CE-ICP-MS, HPLC-ICP-MS, theranostic nanomaterials

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KTH-2 Green sample preparation methods for further determination of metals and non-metals by atomic spectrometric techniques

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Trace element determination has been performed in order to provide information about the influence of elements in several fields such as nutrition, health, toxicology, environment and technology. In spite of the technological developments in instrumentation, especially for atomic spectrometric techniques, samples are generally introduced in the equipment as a solution in routine analysis. Classical methods are generally used for sample digestion and involve the use of a relatively high volume of concentrated reagents and take a long time for digestion. The use of concentrated reagents may require a dilution step of digests before the analyte determination, which could compromise the limits of detection. In addition, some systems present limitations for complete digestion of many matrices. In this sense, even using methods based on microwave- assisted closed vessels, some drawbacks can occur and incomplete digestions are frequently reported. Nowadays, there is a trend for the development of green analytical methods, which require lower reagent consumption and waste generation, less analytical steps combined with high- efficiency digestion. The suitability of the digests with the determination techniques are also important. On this aspect, the main trends for sample preparation for a variety of matrices (such as cosmetics, food and biological samples) will be presented in this lecture for further metals and also non-metals determination by atomic spectrometric techniques. The use of diluted solutions, using systems assisted by microwave and UV radiations or using combustion systems, will be covered. Therefore, recent applications will be presented showing the advantages of methods using diluted reagents for the determination of metals and non-metals using atomic spectrometric techniques.

Keywords: sample preparation, UV radiation, microwave, assisted digestion, microwave, induced combustion, metals determination, non, metals determination, ICP-MS, ICP-OES.

The author is a laureate of the JAAS Emerging Investigator Lectureship 2018

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KTH-3 Atomic pathology: the past, present and future of elemental imaging in medical research

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In this talk, the evolution of elemental imaging using laser ablation inductively coupled plasma mass spectrometry, from its origins in the earth and environmental sciences to its current status as a versatile tool for medical research, will be summarized and major advances from around the world highlighted. The latest developments in imaging technology and its applications in medical and biological research will be discussed and in the spirit of looking to the future made possible by the honour of the *Spectroscopy Magazine* Emerging Leader award, the vast and varied directions elemental imaging will take over the coming years will be a primary focus. While biologists view proteins, lipids, carbohydrates and nucleic acids as the building blocks of life, the chemical elements represent the fundamental constituents of a living organism. Cell types, biological functions and even disease processes have unique elemental signatures. In cases where minor and trace elements are directly implicated in the mechanism of a disease, this signature can be stark, while other scenarios can arise where subtler changes are apparent. The emerging potential as a tool for clinical pathology will be discussed, highlighting how concurrent advances in technology, image analysis, machine learning, and a growing appreciation that the chemical elements are not regulated in isolation are converging to position elemental imaging as a valuable resource for digital pathology and the decision-making process in treating chronic disease.

Keywords: elemental imaging, laser ablation, inductively coupled plasma, mass spectrometry, pathology

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KTH-4 Absolute isotope amount ratio measurements by MC-ICP-MS

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Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is a powerful tool for obtaining high accuracy and precision isotope ratios in a wide range of applications, from the study of age of solar system to studies in archaeology, provenance studies, medical science, nuclear and forensic sciences, geosciences, and environmental science etc. **[1-2]**. Despite this, very few absolute isotope ratio measurements by MC-ICP-MS have surpassed the traditional thermal ionization mass spectrometry (TIMS) because MC-ICP-MS suffers significantly larger isotopic fractionation effects (mass bias) compared to TIMS and efforts to address these effects are not trivial **[3].** Although the majority of the bias can be modeled using mass-dependent laws, mass-independent fractionation (MIF) has been reported in MC-ICP-MS itself for many elements including Nd4-7, Ce5, W8, Sr5, 9, Ge10, Pb10, Hg10, Si11, Ba12 and Os13. Consequently, proper mass bias correction is crucial when MC-ICPMS is used for the determination of absolute isotope ratios. Two state-of-the-art mass bias correction models **[2]** which are capable of correcting both mass-dependent and mass-independent fractionation will be presented and discussed in detail in this lecture. One is a primary method, so called full gravimetric isotope mixture (FGIM) model, which is based on use of all near–pure isotopes of an element (e.g., all four isotopes of ^{204}Pb, ^{206}Pb ^{20,7}Pb and ^{208}Pb) with known chemical purities to prepare gravimetric mixtures, without rely on any existing isotopic standards. The most importantly, FGIM model, does not require prior knowledge of isotopic composition of the near-pure isotopes used. The second model is the optimized regression model and it presents as an alternative secondary method for absolute isotope ratio measurements. This method allows calibrating isotope ratios of an element using a known isotope ratio of another element without assuming that the two elements must necessarily display identical mass bias.

Keywords: isotope ratio, isotope fractionation/mass bias, mass dependent fractionation, mass independent fractionation, MC-ICP-MS

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KTH-5 Non-contact mass spectrometry of adhesive compounds on heat sensitive surface using temperature- controllable plasma jet

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In recent years, several analytical devices of ambient desorption/ionization mass spectrometry (ADI-MS) based on atmospheric plasma such as direct analysis in real time (DART) has been developed and applied for the direct analysis of surface adhesive compounds. However, it is difficult to apply this method to heat-sensitive surfaces because of its high temperature plasma gas (250 ˚C or higher). In our group, the atmospheric plasma soft ablation method (APSA) has been developed as a plasma ADI-MS. In APSA, compounds on the surface are desorbed and ionized simultaneously by reactive species in a low temperature (40-70 ˚C) plasma, which does not give thermal or discharge damage to the surface. This technique allows non-contact and non-invasive analysis of chemicals. Some samples were successfully analyzed with excellent detection limits of pmol order using this method. However, sample desorption efficiency is relatively low because of little thermal desorption due to its low gas temperature. To overcome this problem, we developed temperature-controllable plasma sources and applied to APSA to realize effective sample analysis.

The typical temperature-controllable plasma source has two flow channels for heat exchange in the metal body. The temperature of the metal body can be changed by flowing fluid for temperature control into a flow channel. The gas temperature can be changed by heat exchange with the body by flowing it to another flow channel. Therefore, by controlling the temperature of the fluid in the constant temperature bath, the gas temperature before plasma generation can be controlled. When the temperature of the control fluid was set at -15 ˚C, the gas temperature at the outlet could be reduced to -3.5 ˚C. The designed device was manufactured using a metal 3D printer since it has a complicated spiral flow path inside. It was shown that plasma of various gas species can be stably generated, and that the plasma gas temperature is proportional to the temperature control fluid. Therefore, it can control plasma gas temperature precisely.

Analytical performance of the as an ADI source was evaluated by analyzing agricultural chemicals. Dried 5 L 0.5% solution of a commercial pesticide malathion on the glass plate was directly probed with argon plasma in atmospheric pressure. Ionized species were introduced into an ion trap mass spectrometer. As a result, protonated molecule of malathion was observed as the characteristic ion peak at m/z 331 even when the plasma gas was almost room temperature 30 ˚C. The relationship between the plasma gas temperature and the signal intensity for monomer ions of agricultural chemicals were measured. Gas temperature of the plasma was gradually changed from 30 ˚C to 100 ˚C. Some chemicals were detected by increasing the plasma gas temperature and it was revealed that the temperature which gives highest monomer ion signal is different for each sample chemicals. Detection limits of malathion when the plasma gas temperatures were 30 and 80
˚C (optimal gas temperature for the detection of monomer ion of malathion) were calculated and they were 4.3 and 0.85 nmol, respectively. From these results, it was demonstrated that temperature-controllable plasma allowed us to choose wide range of analyses in terms of analytical sensitivity and thermal stress to the substrate.

Device and results of non-contact mapping analysis device for skin surface compounds using low power laser and low temperature plasma will also be presented.

Keywords: ADI-MS, atmospheric plasma, temperature, controllable plasma

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OTH-01 The isotopic challenge: metrological approaches for accurate isotope measurements

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The recent progress in the development of multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has resulted in an improved instrumental precision and a substantial increase of sensitivity (considering e.g. the introduction of amplifiers with 10E13 resistors and improved (in terms of stability and sensitivity) sample introduction systems). As a consequence, even minor differences in the isotope-abundance ratio measurements can be monitored. Simultaneously, analytical errors, which were before hidden in the measurement uncertainty, have become crucial factors and extreme caution has to be taken to avoid drawing conclusions from analytical artefacts. Asides the fact that approaches for accurate isotope ratio determination have to be reconsidered, also previously established approaches must be adapted to modern metrological foundations. In addition to the persistence of historical practices, fundamental metrological principles are often unknown or simply ignored, arguing that it has always been accomplished and become routine and accepted, so far. Thus, harmonized wording and nomenclature as well as calculations based on internationally agreed principles are a prerequisite for good scientific practice, as well. This is evident in order to make accomplished data internationally comparable and traceable. We clearly demonstrate that the different applied approaches generally presented for the measurement of the isotopic composition of even a "simple isotopic system" such as Sr leads to substantial differences and misleading results. Moreover, the different 'historical' calculation approaches provide different sets of data with different meaning, which is usually not clearly stated in scientific publications.

In order to provide accurate and comparable data, proper calibration of the isotopic composition has to be accomplished. We explicitly show within this contribution, that the improved instrumental performance has made it evident to reconsider internal correction protocols for instrumental isotopic fractionation (IIF; aka "mass bias") e.g. for Zr on Sr or Tl on Pb. Similar, correction for isobaric interferences has to consider different IIF correction factors for different elements. Recent papers have demonstrated that mass independent fractionation (MIF) in modern mass spectrometers just cannot be simply ignored. In addition to the commonly believed mass- dependent fractionation (MDF) phenomenon, recognition and reporting of mass-independent fractionation within MC-ICP-MS itself has proliferated in the last decade. As a consequence, the use of mass-dependent correction models can result in biased isotope-amount ratios. Moreover, the lack of suitable reference materials has become a further crucial and limiting factor. We demonstrate that for a number of reference materials a recertification has to be considered to cope with state of the art demands in isotope research.

In addition, isobaric and polyatomic interferences as well as the influence of the matrix on the instrumental isotopic fractionation factors have rendered evidence that a quantitative analyte/matrix separation is a prerequisite for sample preparation. Moreover, improved instrumental sensitivity has made the chemical blank a crucial factor especially when considering the general uncertainty of an isotopic measurement. As prominent examples, B, S and Zn are isotopic systems where a proper blank correction has to be considered accordingly.

In general, it can be observed, in recent literature, that appropriate uncertainty calculation is frequently not accomplished and repeatability (intermediate precision) or even standard errors of the mean are "sold" as uncertainties. Via selected examples, the impacts of such misleading calculations on the accurate isotope ratio calculation within different systems is shown..

In consequence, profound knowledge and application of metrological principles is more than ever required, considering the exponential increase of available analytical data and the need of long term comparable data sets.

Keywords: MC-ICP-MS, isotopic analysis, uncertainty calculation, mass bias

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OTH-02 Cold plasma: way to improve repeatability of metal analysis in sub-microliter volumes?

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Substrate-assisted laser desorption inductively coupled plasma mass spectrometry (SALD- ICP-MS) allows fast and direct determination of metals in sub-microliter volumes applied onto a polymer substrate in the form of dried droplets. In certain cases, however, RSD values range up to 30 % due to the formation of inhomogeneous dried droplets.

The addition of a suitable internal standard and incorporation of diffuse coplanar surface barrier discharge (DCSBD) for surface treatment of substrate improve the repeatability of the determination considerably. DCSBD treatment of substrate surface allows increasing its wettability, which results in the formation of homogenous dried droplets. However, a disadvantage of this treatment is the occurrence of the "aging" effect, *i.e.* a gradual regression of the modified physical- chemical properties of the substrate surface to an original state.

An extensive set of experiments was designed to examine the effectiveness of DCSBD treatment of plastic substrates and aging effect. First, Polyethylene Terephthalate Glycol (PETG), Polyethylene Terephthalate (PET), Polycarbonate (PC) and Styrene Acrylonitrile (SAN) substrates were exposed to DCSBD by 1, 5 or 10 s at 400 W (RPS400-Roplass plasma system 400 W, Roplass, Czech Republic). Then, the samples of cell lysates, culture medium and 0.5 mmol.L^{-1} sodium citrate with the addition of copper and cadmium as representatives of significant metals monitored in an organism and environment were added to the samples. Furthermore, nickel and indium were used as internal standards. The samples were applied immediately, 1, 3, 7, 30, 90 or 180 days after the substrate treatment. A contact angle and diameter of the dried droplets were measured for all droplets (See System E, Advex Instruments, Czech Republic). The dried droplets were desorbed with 213 nm Nd:YAG pulse laser (UP213, New Wave Research, USA) and ^{60}Ni, ^{63}Cu, ^{111}Cd and ^{115}In isotopes were analysed by an ICP quadrupole mass analyser (7500ce ICP-MS, Agilent, USA).

The experiments have shown a significant change in the wettability of the substrates with DCSBD treatment. The repeatability of the determination is considerably better for the samples applied to the substrates in the shorter time interval from DCSBD treatment. But, the type of the substrate, its treatment and aging effect as well as sample composition, influence significantly repeatability of the determination.

Keywords: surface, assisted laser desorption inductively coupled plasma mass spectrometry, SALD-ICP-MS, diffuse coplanar surface barrier discharge, DCSBD, repeatability, submicroliter volumes, internal standard

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OTH-03 Copper isotopic composition as a biomarker for liver cancer : a large cohort study

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Since now more than ten years, a new tool is investigated to monitor copper status of patients with the introduction of copper isotopic measurements **[1]** done with very high precision mass spectrometer MC-ICP-MS. These MS were originally developed for geological applications and were also used for food tracing. Measuring copper stable isotopic composition on biological samples and fluids was investigated and measurable variations were detected and correlated to cancer status of patients in 2015 **[2]**. Some first works on liver cancer were done with a follow up study **[3]** which has shown good correlation between isotopic composition and patient liver status.A large scale clinical study on liver cancer was started in 2015 in Lyon with the "La Croix Rousse" hospital to evaluate the potential application of these isotopic variations as a biomarker. After measuring more than 200 healthy patient, we will present more than 400 samples from patients with hepatitis B and C, cirrhotic liver status or NASH with and without hepatocarcinoma. Other samples were also obtained during another clinical study with cancer patient treatment by radiofrequency. These results show good correlation with the liver status but also permit to better understand all the phenomena needed to understand before making a clear diagnostic using copper isotopic composition.

Keywords: isotopes fractionation, copper, liver cancer.

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OTH-04 Matrix matched validation procedure for single cell measurements with automatized-flow injection

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A growing number of engineered nanomaterials (NMs) is being used in consumer products, in cosmetics. As a result, their potential to enter biological systems might possibly represent an increasing risk of adverse effects to humans. The hazardous potential of NMs depends on their properties, such as composition, size, shape, presence of ligands or coatings, as well as the possibility to release ions. In toxicology, the total amount of metals taken up by organisms or cells is an important factor for potential adverse effects. The qualitive and reliable detection of metals contained in single cells is challenging due to the low amounts (ag-fg) of analytes. Depending on the element of interest, high background levels including matrix interferences exist which lead to a reduction of the sensitivity for a respective analyte. In this study, we are looking for an optimized matrix matched single cell ICP-MS method to: i) increase the sensitivity for aluminum (Al), ii) decrease the detection limit, iii) estimate the total amount of aluminum (Al) nanomaterials absorbed by cells. Therefore, the ICP-MS was optimized using a matrix matched full instrumental tuning approach. Here, validations for different ICP-MS measurement modes (*e.g.* collision cell mode combined with continuous and single cell mode) and injection systems (with full automated sample uptake) were performed with analyte concentrations close to the detection limit. Overall the detection limit was improved significantly. In addition, the Al NM concentration per cell was determined at low number concentrations of 1 – 100 NMs per cell.

Keywords: single cell ICP-MS, matrix, match, method development

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OTH-05 Determination of Fe isotopic composition using MC-ICP-MS for the elucidation of the iron uptake mechanisms in yeast mutants

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Iron (Fe) is an essential trace element which plays important role as a cofactor in many metabolic processes occurring in living organisms. The analysis of Fe isotopic composition by MC- ICP-MS is a new analytical approach for metabolomics enabling better understanding of the mechanism of Fe uptake by living organisms **[1-3]**. Characterization of the Fe uptake machinery, and then its distribution and storage is a major challenge to understand how Fe homeostasis is maintained within plants. In the course of evolution, plants have developed two strategies for Fe uptake. Strategy I is based on the reduction of Fe^{3+} ions to Fe^{2+} ions and their subsequent transport to the root cells. Strategy II consists in chelating of Fe^{3+} and transporting the phytosiderophore(PS)- Fe^{3+} complex to the root. It is supposed that the type of Fe uptake strategy directly influences on the formation of distinctions in Fe isotopic ratios in living organisms **[4,5]**.

The aim of this study was the optimization of analytical method for the determination of the Fe isotopic composition in yeast *Saccharomyces cerevisiae* (a simple single-cell model organism which is extremely well-characterized for its Fe acquisition machinery) using MC-ICP-MS and to investigate the relevance of using Fe isotopic signature for elucidation of its uptake mechanisms. Two types of mutants were used for the study: one expressing only the Fe^{2+} ionic pathway for the Fe uptake (similar to the Fe^{2+} uptake by Strategy I plants), whereas the other expresses only the chelated way with a specific uptake of Fe(III) bound to desferrioxamine (mechanism similar to the Fe(III)-PS complex uptake by Strategy II plants). The method, including careful matrix removal was optimized using bakery yeast *Saccharomyces cerevisiae* purchased on the local market.

The variability of ^{56}Fe and ^{57}Fe for both mutants (^{56}Fe = -0.67 ‰ and ^{57}Fe = -1.00 ‰ for type I and ^{56}Fe = -0.31 ‰ and ^{57}Fe = -0.35 ‰ for type II) in relation to the Fe isotopic composition determined in nutrient solution of iron (^{56}Fe = 0.17 ‰ and ^{57}Fe = 0.29 ‰, 2SD= 0.06‰) was observed. It indicates the occurrence of isotopic fractionation resulting from biochemical transformations taking place in the organism, conditioned by the type of Fe uptake mechanism. The presence of lighter Fe isotopes for mutant type I, compared to the mutant type II, confirms the existence of the ionic mechanism of Fe collection for mutant type I and chelated way for mutant type II.

Keywords: MC-ICP-MS, iron, isotopic composition, yeast mutants

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OTH-06 Plasma-based techniques: a versatile tool to gather insights into lithium losses of lithium ion batteries

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Since its introduction in the early 90's, the lithium ion battery (LIB) has to face challenging demands for mobile and stationary applications, respectively. The negative electrodes of the state-of-the-art LIBs are based on carbonaceous material delivering a decent capacity of 372 mAh.g^{-}[1]. Lithium transition metal oxides ($LiMO_2$; *M* = Mn, Co, Ni) are used as positive electrodes supplying capacities in the range of 150 mAh.g^{-1} like ternary mixtures of nickel, cobalt and manganese ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111)). However, these materials suffer from fading capacities
- especially at elevated charging cut-off voltages exceeding 4.4 V - which cause is still a matter of discussion in literature **[1,2]**.

One postulated degradation mechanism is assigned to the passivation layer on the carbonaceous negative electrode, which is called the solid electrolyte interphase (SEI). It is formed during the first cycle due to the high reductive potential affecting the electrolyte and consuming active lithium (either from the conducting salt or the cathode material). Furthermore, the kinetic hindrance of lithium re-insertion into the transition metal oxide host structure is another debated mechanism **[1,2]**. In order to quantify the lithium loss in both positive and negative electrodes, plasma-based analytical techniques are well suited for these investigations.

In this work, inductively coupled plasma optical emission spectroscopy (ICP-OES) is used to investigate the lithium loss in charge/discharge aged layered NCM-based cathode materials as well as the lithium loss in carbonaceous anodes using glow discharge sector field mass spectrometry (GD-SF-MS). Additionally, investigations of ^{6}Li-isotope enriched cathode materials were conducted using inductively coupled plasma mass spectrometry (ICP-MS) and GD-SF-MS for bulk and depth- resolved quantification of lithium losses in charge/discharge aged LIBs. Therefore, a NCM111 material is synthesized using ^{6}Li-enriched components as source material and cycled in a full-cell set-up to elucidate the origin of lithium losses. With this approach, it is possible to distinguish between losses either from the conducting salt or the cathode material for tailoring future LIBs.

Keywords: lithium ion batteries, lithium loss, glow discharge

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OTH-07 Triple isotope fractionation exponents of elements measured by MC-ICP-MS: an example of Mg

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In chemical elements with three or more stable isotopes (for example, isotopes x, y, and z), mass-dependent stable isotope fractionation yields correlated isotope ratios, my/mx and mz/mx. In three-isotope space, i.e. in a "my/"mx vs. "mz/"mx plot, data align along a slope , the so-called "triple isotope fractionation exponent" that scales the two isotope ratios. Theoretical calculations predict small but significant differences in for kinetic- and equilibrium isotope fractionation mechanisms **[1]** and thus the precise measurement of allows one to constrain the reaction mechanism. However, due to an apparent lack of precision of stable isotope analysis by MC-ICP- MS, is currently used merely as analytical quality control, i.e. for demonstration that samples and standards plot within their analytical precision in the range of theoretical values originating in zero.

Here we show how can be determined precisely enough by MC-ICP-MS to distinguish kinetic and equilibrium isotope fractionation. We determine quality standards regarding interferences and measurement conditions to ensure trueness and to maximize precision. As an example, we explore the measurement of the triple-isotope fractionation exponent of Mg, budget the uncertainty of values, and report the first values of carbonate-water pairs and bioapatite. The capability to measure values more precisely adds a new dimension to isotope data beyond the scale, and thus has a high potential to reveal different modes of abiotic and biotic mineral precipitation today and through the geological record, thus helping to resolve outstanding conundrums in the Earth and Life Sciences.

Keywords: three isotope plot, kinetic isotope fractionation, equilibrium isotope fractionation

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OTH-08 Optimization possibilities for difficult matrices with ETV-ICP-OES

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For determination of element concentration as well as element-species for solid samples different techniques are available, for example X-ray fluorescence spectroscopy (XRF), ICP-OES or –MS, neutron activation analysis (NAA), X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (REM-EDX) or infrared spectroscopy (IR). Most of them are time-consuming methods, which need previous preparation steps like ashing or digestion of samples whereby a sample alteration could take place.

The method of electrothermal evaporation in combination with inductively coupled plasma and optical emission spectroscopy (ETV-ICP-OES) enables simultaneous analysis of a large number of elements quantitatively as well as qualitatively in a wide range of concentration (ppb - %), without previous sample treatment, except for homogenization. The solid sample can be vaporized in a graphite oven at temperatures up to 3000 °C in short analysis times. The vaporized sample will be introduced into the plasma as a dry aerosol by an argon gas stream and the assistance of a reaction gas. Especially for samples which are difficult to digest, this method is a suitable less time consumable alternative. Owing the freely adjustable temperature program the temperature/time dependent release of elements can be observed, which partly allows for conclusions regarding the binding characteristics and the chemical association of some elements. The suitability of ETV-ICP- OES for different sample matrices (plastics, copper, biomass, coal) has been shown in various papers. Nevertheless some matrices turn out to be more difficult in analysis than others, such as geological samples, sediments or glasses, because of their special evaporating behavior and resulting high load of the plasma caused by sample matrix. Not only the high temperature needed for complete vaporization may pose a problem, but also the reproducibility of results. Considering physical, chemical and technical possibilities in case of ETV-ICP-OES starting with sample preparation, temperature treatment, variation in modifier gases and plasma conditions there are many ways for optimization.

On the basis of several standard materials with difficult matrices some of the optimization possibilities are shown and tested on real samples. The results are compared with established analysis methods.

Keywords: ETV-IC- OES, method optimization, evaporating behavior, sediment, glass

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OTH-09 Accurate determination of lithium and boron isotope ratios by MC-ICP-MS with normalisation to an internal standard

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Variations in stable isotopic composition of lithium and boron are commonly expressed as ^{7}Li and ^{11}B values, respectively, and are widely used in geochemistry and environmental sciences. Although a plethora of instrumental techniques allows determination of Li and B isotope ratios, MC-ICP-MS gets increasingly popular for highly precise and accurate measurements. One of the major issues in the isotopic analysis of Li and B by MC-ICP-MS comes from the need to correct appropriately for instrumental mass discrimination, which is demonstrated to be the largest for light elements. Sample-standard bracketing (SSB) is the correction model used almost exclusively for this purpose in the case of lithium and boron **[1]**. Random fluctuations in the plasma and matrix effects, induced by minor differences in the chemical composition between sample and standards, represent a significant hindrance to precision and accuracy of the measurements. It is known that the technique of SSB as a sole means of correcting for instrumental mass discrimination can lead to biased results if the chemical compositions of isotope standards and samples are not identical.

This lecture will describe new methodology that makes possible for the first time the determination of both Li and B isotope ratios in a single measurement with online normalisation to ^{26}Mg/^{24}Mg isotope ratio of admixed internal standard. This normalisation was found to be effective in correcting for drift in instrumental mass discrimination as evidenced by the results of ruggedness testing using the Plackett-Burman factorial design. Typical standard uncertainties associated with ^{7}Li and ^{11}B values for carbonate minerals, samples of roasted coffee and synthetic solutions determined by the new method were 0.3‰ and 0.4‰, respectively. An important advantage of the method is that it allows determination of SI traceable $n(^{7}\text{Li})/n(^{6}\text{Li})$ and $n(^{11}\text{B})/n(^{10}\text{B})$ isotope amount ratios by using isotopically certified Mg standards and the regression model of correcting for instrumental isotope fractionation. Thus the developed method offers a cost- and labour effective independent calibration approach for $n(^{7}\text{Li})/n(^{6}\text{Li})$ and $n(^{11}\text{B})/n(^{10}\text{B})$ isotope amount ratios which can be used for the characterisation of isotopic reference materials.

Keywords: calibration, isotope amount ratios

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OTH-10 Critical evaluation of optical spectrometry vs mass spectrometry for stable isotope analysis

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Mass spectrometric methods (MC-ICP-MS and TIMS) are, without doubt, the working horse of stable isotope analysis. However, drawbacks of these methods include the high costs for instruments and their operation, experienced operators and elaborate chromatographic sample preparation which are time consuming.

Optical spectrometric methods are proposed as faster and low-cost alternative for the analysis of isotope ratios of selected elements by means of high-resolution continuum source molecular absorption spectrometry (HR-CS-MAS) and laser ablation molecular isotopic spectrometry (LAMIS) **[1,2].** First, stable isotope amount compositions of boron (B) and magnesium (Mg) were determined based on the absorption spectra of *in-situ* generated heteronuclear diatomic molecules (MH or MX) in graphite furnace HR-CS-MAS. The use of a modular simultaneous echelle spectrograph (MOSES) helps to find the maximal isotope shift in the diatomic molecular spectra produced in a graphite furnace by using isotopic spike solutions **[3].** Isotopes of boron (^{10}B and ^{11}B) were studied via their hydrides for the electronic transition $X1 + A1$. The spectrum of a given sample is a linear combination of the ^{10}BH molecule and its isotopologue ^{11}BH. Therefore, the isotopic composition of samples can be calculated by a partial least square regression (PLS). For this, a spectral library was built by using samples and spikes with known isotope composition. Boron isotope ratios measured by HR-CS-MAS are identical with those measured by mass spectrometric methods at the 0.15 ‰ level. Similar results were obtained for a multiple isotope system like Mg (^{24}Mg, ^{25}Mg, and ^{26}Mg), where isotope shifts of their isotopologues can be resolved in the MgF molecule for the electronic transition $X2$ $A2$ *i*. Finally, the application of molecular spectrometry via emission by LAMIS is compared and discussed **[4]**.

Keywords: stable isotopes, MC-ICP-MS, HR-CS-MAS, LAMIS, diatomic molecules, boron, magnesium

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OTH-11 Developing low-volume solution ICP-MS for high-precision uranium isotope analysis

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Analysis of uranium isotopes in geological, environmental or nuclear materials requires consideration of the amount of waste produced, material required, and the precision needed for the study. These are in part limited by the conventional dry plasma sample introduction technique. Overcoming these problems may be achieved by use of low-volume solution sample introduction ICP-MS method, a technique which utilises smaller volumes of total solution to pre-concentrate the analyte of interest.

Due to an increased signal to noise ratio, the potential advantages to low-volume solution ICP-MS as demonstrated on Lu-Hf by Bauer and Horstwood (2018), include an increased precision for a given amount of uranium when compared to the conventional dry plasma techniques, or a reduction in the amount of uranium required to achieve the necessary precision. When applied to the micro-sampling of materials, this potentially increases the spatial resolution achievable or opens the door to analysis of novel materials with concentrations of analyte previously too low to measure. Low volume analysis also produces negligible sample waste and decreases the time taken per analysis.

We are currently developing and improving the technique of Bauer and Horstwood (2018) to investigate the benefits of low-volume sample introduction on analysing uranium. Utilising the Teledyne-CETAC MVX 7100 l Workstation, coupled with a ThermoScientific Neptune Plus MC- ICP-MS and Nu AttoM SC-SF-ICP-MS, preliminary results currently demonstrate measurement uncertainty of 0.0176% (2SE) at 2 ng uranium. This is a 50% improvement in precision over dry plasma methods, with further improvements expected. Blank contributions for uranium using this approach are negligible.

These results show the promise of a new ICP-MS sample introduction technique that has the potential to increase safety when handling uranium-bearing materials due to the lower sample sizes required, and the negligible sample waste produced. This technique may also yield insights into U isotope fractionation at the single mineral grain scale, a measurement which was previously unobtainable.

Keywords: ICP-MS, low volume, uranium, MVX, nuclear, geology, environment, sample introduction, precision

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OTH-12 Changes of size-resolved element distributions in particulate matter induced by New Year's Eve fireworks

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New Year's Eve fireworks are a unique source of atmospheric pollutants in the course of a year. Pyrotechnic articles contain a variety of metal salts (*e.g.* Li, Na, K, Ca, Cu, Rb and Sr) as chlorates, perchlorates and nitrates and their extensive use leads to an accumulation of these metals in the atmosphere within a short span of time. Chemical characterization of firework aerosols is important, because these events give rise to extremely high levels of respirable particles inducing negative health effects like cardiopulmonary diseases or asthma **[1]**.

In order to examine metal accumulation in the atmosphere due to New Year's Eve fireworks more closely, we collected airborne particles in 14 size fractions in the range from 15 nm to 10 µm, in two European cities (Brno, Czech Republic and Graz, Austria) in two consecutive years, using an electrical low pressure impactor (ELPI+, Dekati Ltd., Kangasala, Finland). Results from 14 days sampling periods including New Year's Eve were compared to results from 14 days sampling periods during normal winter weeks. After microwave-assisted acid digestion with nitric acid using an ultraCLAVE III digestion system (MLS GmbH Mikrowellen-Labor-Systeme, Germany) and determination of element content on an Agilent 8800 triple quadrupole ICP-MS/MS (ICP-QQQ, Agilent Technologies Japan), distribution patterns for 33 different elements in the particle sizerange from 15 nm to 10 µm were determined.

By combining the sampling of size-resolved respirable particles using ELPI+ with subsequent analysis of samples by ICP/MS, we are able to show a firework specific change of distribution patterns for a series of elements closely related to pyrotechnic activities. The behavior of color-giving elements Mg, Al, K, Cu, Ba and Bi will be discussed with respect to their distribution in the different size fractions.

Keywords: ICP-MS/MS, fireworks, elemental composition, respirable particles, particulate matter

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More misnomers, misconceptions and musings in ICP spectroscopy

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Yet again, this talk describes recollections frrom the early days of both ICP emission spectroscopy and ICP-MS. Certain key concepts in these methods, such as why there are MO^+ ions in ICP-MS, are often misstated, to the point of being accepted. Fundamental causes of interferences will be emphasized. Successful analysis boils down to the basic properties of the ICP, which is still unrivalled.

Keywords: ICP, ICP-MS, interferences

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THP-1 Provenancing of fish via elemental and strontium isotopic analysis of hard and soft tissues by (MC-) ICP-MS

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The demand for reliable methods to determine the origin and authenticity of fish has been increasing steadily for the last years. In particular, consumers are claiming for a clear declaration and strict controls of indication of origin. In order to proof origin and authenticity and to countervail fraudulent practices, elemental and isotopic analyses have been developed and applied as very useful tools. The n(87Sr)/n(86Sr) isotope ratio is a particularly well-suited indicator of geographic origin of fish due to geologically related regional differences. Fish take up Sr and other trace elements from the water mainly through the gills but also via the feed. The chemical information is incorporated into hard and soft tissues. Soft tissues store the recent chemical information following the chemical turnover, while incrementally growing hard tissues, such as otoliths, incorporate atime resolved information of the life span of a fish. Within the scope of the project 'CSI: TRACE YOUR FOOD', n(87Sr)/n(86Sr) isotope amount ratios and the multi elemental composition of different hard parts and soft tissues of fish from lakes and fish farms in Austria were analyzed together with ambient water and fish feed using (multi- collector) inductively coupled mass spectrometry ((MC-) ICP-MS). The Sr isotope ratio in otoliths and fish bones could be identified as main chemical parameter in order to classify fish with respect to the geographical origin. The n(87Sr)/n(86Sr) isotope ratio of fish filets could be assessed to provenance the origin. The isotopic composition in the fillet showed an influence of both water and ingested feed. The additional use of elemental pattern (Sr/Ca, Mg/Ca, Na/Ca as well as Cu, Zn, Fe, Co, Mn) improved the identification of provenance.

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THP-2 Determination of lead isotope ratios in Antarctic snow by quadrupole ICP-DRC-MS using a total- consumption sample introduction system

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The determination of Pb isotope ratios in snow and ice from polar areas can provide useful information on the sources of both natural and anthropogenic atmospheric inputs, the relative contributions of these sources over time and the corresponding transport routes. However, precise and accurate determination of isotope ratios is quite challenging, due to the low lead concentration occurring in these matrices (typically at the pg.g^{-1} level), thus requiring ultra-clean collection, storage and treatment procedures. In addition, the limited amount of sample typically available can prevent the application of efficient preconcentration approaches and the identification of short time- scale events. Finally, these studies generally make use of high-priced instrumentation, such as thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), whereas cheaper techniques such as quadrupole ICP-MS would be advantageous.

In order to overcome these limitations for the analysis of snow samples, we applied a simple preconcentration procedure based on freeze-drying in combination with quadrupole ICP-MS equipped with a total consumption sample introduction system **[1,2]**. This apparatus, called torch- integrated sample introduction system (TISIS), consists of a PFA micronebulizer mounted onto a heated single-pass evaporation chamber, with a sheathing gas stream protecting the aerosol from impact against the chamber wall. The main advantages of this system include an increase in sensitivity and the capability of working at very low sample consumption rates (20 L.min^{-1}), allowing to preconcentrate the samples to small volumes (200 L) and so achieving high preconcentration factors. In addition, neon was used in a dynamic reaction cell to improve the precision by collisional damping.

Under the optimal conditions, internal precision, expressed as relative standard deviation, varied from 0.12 to 0.18% (c=10 g.L^{-1}; n=12), while the external precision was < 0.1%. The potential influence of the pre-concentration procedure on the analytical data was carefully investigated in terms of blank contribution, recovery and isotopic fractionation. The developed method was finally applied to the analysis of Antarctic snow samples previously characterised by multi-collector ICP-MS, obtaining a satisfactory agreement between the two techniques.

Keywords: antarctic snow, microsamples, dynamic reaction cell, inductively coupled plasma mass spectrometry, isotope ratios

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THP-3 Isotopic and multi-elemental signatures as indicators of origin of sparkling wines

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The quality of food is a highly important subject worldwide. Despite of this fact, frauds have always existed especially in the luxury market. In this economical sector, the identification of wine fraud is one of the most important and challenging issues facing the wine industry. Tracing the geographical origin and authenticity of wines allows to detect false description of origin and mislabeling.

In order to determinate Champagne wines authenticities and counterfeit products, both multi-elemental analysis Sr and Pb isotopic ratios were determined in 31 sparkling wines from France, England, Italy, Portugal and Spanish. Major (Na, K, Ca and Mg) and trace elements (Li, B, Al, Sc, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba, Pb and U) were measured by quadrupole ICP-MS. A methodology for the precise and accurate determination of the Sr isotopic ratios in sparkling wine was developed using MC-ICP-MS while Pb isotopic composition was determined by HR-ICP-MS.

These combinations of analysis allowed to separate the Champagne from sparkling wines coming from other countries and address distinctive elements important for the discrimination of wine categories and origins.

Keywords: sparkling wines, counterfeit products, Sr isotopic ratio, authentication

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THP-4 Tracing the geographical origin of food products with multielement fingerprinting, isotope ratios and chemometrics: the case of Rocha pear

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Rocha pear (Pyrus communis L. var. Rocha) is a traditional Portuguese variety of pear recognized by its organoleptic qualities. Adding to the known benefits of consuming fruit in general, pears are considered a good source of fiber and potassium with low sodium content, combined with low glycemic index **[1,2]**. The nutritional value of pears, in particular its mineral content, is of great relevance for human nutrition and public health. In this sense, Food Composition Databases (FCDBs) are a crucial tool. In this study, we analyze the mineral content of Rocha pears to promote the linkage between the nutritional profile and geographical origin, filling the gap of absent values in FCDBs.

Rocha pears produced in the west part of Portugal can be certified as Protected Designation of Origin (PDO), under the label of "Pera Rocha do Oeste". These represent the largest PDO production in the country **[3]**. However, this variety is also cultivated in other areas at national level (nPDO) and is gaining interest at international level due to growing exportations.

The mineral profile of plants is a reflection of the soil type and the environmental conditions under which plants were grown. Therefore, minerals and trace elements, as well as their isotopes, are expected to be suitable biomarkers in authenticity studies **[4,5]**. Nonetheless, to extract the most information from datasets these must to be combined with chemometric tools capable of performing multivariate data analysis.

The present work aims to develop a chemical fingerprint of Rocha pears produced within the PDO region based on multielement analysis and isotope ratios (IR). For such purpose, 150 pear samples were collected from 10 farms located in two regions (PDO and nPDO). Samples were analyzed in pools, each composed of 3 pears from the same tree, leading to 50 pools. Multielement analyses were carried out, in triplicate, in compliance with NP EN ISO/IEC 17025 and EN 1380. The content of twenty-four minerals and trace elements was measured by inductively coupled plasma optical emission spectrometer (ICP-OES) (Fe, Mg, P, Ca, Na, K) and ICP mass spectrometer (ICP-MS) (Li, Be, B, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Tl, Pb). A Multicollector ICP-MS (MC-ICP-MS) was used to determine Sr IR.

Results showed a low level of the analyzed contaminants indicating that these do not present a risk for consumers. K was the most abundant element, followed by P. Be, Se, Sn and Pb were systematically below the limit of quantification (LOQ) and were not included in the statistical treatment. The dataset for multielement content and Sr IR was analyzed resorting to chemometric techniques, namely Principal Component Analysis (PCA), Hierarchical Clustering Analysis (HCA) and Linear Discriminant Analysis (LDA). Differences were identified in the level of inorganic components between the regions under study. The most significant were in the levels of Al, Ni and Na, which were higher in samples originating from the PDO region, while the content of Sr and Tl were superior outside this region. The exploratory analysis, based on the unsupervised models PCA and HCA, identified relationships between samples and their geographical provenance. LDA confirmed the possibility of tracing pear samples to the correspondent origin based on mineral profile and Sr IR. Samples used for cross validation of the predictive model were matched to its origin with 100% accuracy.

In conclusion, the analytical methods were suitable for the purpose and are recommended methods for the analysis of inorganic components even at low values. The chemometric techniques used allowed the differentiation of samples according to their geographical origin, contributing to its authenticity and traceability as well as to a deeper knowledge of the mineral content of Rocha pear. The combination of these two techniques is a proper tool for mineral fingerprinting of Rocha Pear's geographical origin.

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Keywords: food analysis, authenticity, Rocha Pear, traceability, inorganic markers, multielement analysis, isotope ratio, chemometrics

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THP-5 Microsampling approaches for isotopic analysis: focus on Wilson's disease patients

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Despite elemental analysis has been long used in clinic, isotopic analysis of biological samples is receiving a growing interest as it might offer valuable information for the early diagnosis and monitoring of several diseases. The development of substantially upgraded multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has enhanced the isotopic analysis of a broader range of samples, especially biological samples. Isotopic analyses generally require at least few milliliters that are injected via a pneumatic nebulizer into the plasma of the ICP-MS. However, in some cases, a smaller amount of sample (few microliters) is available or can be collected (like for new-born screening, therapeutic drug monitoring, etc.), underscoring the urgency of developing new methodologies. The implementation of microsampling techniques based on dried matrix spots (DMSs), such as dried blood spots (DBSs), dried urine spots (DUSs), dried plasma spot card (DPS) or volumetric absorptive microsampling (VAMS) coupled to alternative sample introduction systems capable to operate with only few microliters of sample (direct micro nebulization, laser ablation and electro thermal vaporization) could deal the current problem.

Wilson Disease (WD) is a genetically determined disorder related with Cu metabolism which accumulates in the body (liver, brain ...). This clinical condition is caused by mutations in the ATP7B gene, which encodes the ATP7B protein. As a consequence, Cu levels in both blood and serum are lower in the WD patients. In some cases, the determination of copper concentration in blood is a difficult task. For example, in new born, due to the immaturity of their liver, trend to have low Cu levels even when they are healthy. Due to the fact that the protein ATP7B interacts with the two natural isotopes of Cu (^{63}Cu and ^{65}Cu), the ^{65}Cu/^{63}Cu ratio of WD blood might be affected differently compared to control patients.

We propose here three new approaches for micro-sample analysis to diagnose and monitor WD. Direct laser ablation of microliter samples, micronebulisation and ETV-MC-ICP-MS have been then evaluated. Results in terms of analytical performance (accuracy, precision, sample throughput and sample volume) will be presented together with results obtain on WD rat blood samples.

Keywords: isotopic analysis, microsampling, Wilson's disease, laser ablation, electro thermal vaporization, micronebulizer,iInductively coupled plasma, mass spectrometry, multicollector

Acknowledgements

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THP-6 Factors determining limits of detection

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In order to detect elements in small quantities, the limit of detection is often used as a parameter to assess the performance of the instrument and method used for the analysis. Hereby, the LOD is defined as the lowest concentration which can be measured with a specified error. One of the easiest and therefore the most frequently used method to estimate the instrument detection limit (IDL) is the three-sigma method. Here, the LOD is defined as the concentration of 3x the standard deviation of the blank sample divided by the sensitivity of the instrument. We investigated the impact of different factors such as laboratory conditions, chemical quality and sensitivity of the instrument on the limit of detection. Working under clean room conditions and highest quality chemical are required if the lowest possible LODs need to be achieved. The all-digital detector and the unmatched sensitivity of the PQMS results in $pg.L^{-1}$ LODs.

Keywords: limit of detection, blanks, sensitivity, laboratory environment

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THP-7 Serum magnesium isotopic signature in type I diabetes

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Magnesium is an essential element in the human body, involved in many physiological processes. It is the second most abundant intracellular cation and the fourth most abundant mineral element in the human body. Mg deficiency occurs in numerous diseases, also in type 1 diabetes. However, the total serum Mg concentration does not reflect an individual's Mg status, and a reduced intracellular or ionized serum Mg concentration can be present with normal total serum concentration. It has been shown that serum isotopic signatures of some mineral elements, such as Cu and Fe, can be valuable in a clinical context however, the Mg isotopic signature has to the best of our knowledge not been explored for this purpose yet. In this work, a method was developed for high-precision Mg isotopic analysis of whole blood and blood serum *via* multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). AG50W-X8 strong cation exchange resin was used for Mg purification. Mg isotopic analysis was performed in several biomaterials, *i.e.* Seronorm™ Trace Elements Serum L-1, Seronorm™ Trace Elements Whole blood L-1 and Seronorm™ Trace Elements Urine L-1 reference materials, and commercially available goat serum, sheep serum, mouse serum and fetal bovine serum for validation purposes. Mg isotope ratios were expressed relative to those in the DSM-3 isotopic reference material and also relative to ERM-AE 143, as an alternative/new isotopic standard. Also, IRMM 009 was characterized against DSM-3. Serum Mg isotopic signatures were investigated in a cohort of patients suffering from type 1 diabetes and compared to those in a reference population (assumed healthy individuals). The serum Mg isotopic signature of diabetic type 1 patients was significantly lighter than that of the reference population. These results pointed towards the suitability of Mg isotopic analysis in a clinical context.

Keywords: Mg isotopes, MC-ICP-MS, Type 1 Diabetes

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THP-8 Strontium isotope ratio used as provenance indicator for milk samples from different regions in Slovenia

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The authentication and verification of the geographical origin of food commodities are important topics in the food sector. Over the last 6 years, an increasing number of studies have been published covering the use of strontium (Sr) isotopes in distinct areas of food studies. Namely, Sr has four naturally occurring isotopes, three of which (^{84}Sr, ^{85}Sr, ^{88}Sr) are stable, and a radiogenic one ^{87}Sr, that is derived from the decay of ^{87}Rb. This means that the $^{87}Sr/^{86}Sr$ ratio of a rock is dependent upon the Rb content. As a result, low-Rb rocks such as basalt will have whole rock $^{87}Sr/^{86}Sr$ values around 0.706 whereas older and more Rb-rich rocks such as granites tend to have much higher values. Generally, light elements such as hydrogen (H) and oxygen (O) have been frequently used to determine food provenance, but these isotopes are affected more than the Sr by other factors, such as diet and climate. The result is that the Sr isotopic composition of a sample yields information about provenance, unobscured by local climate variations or biological processes (animal metabolism).

Slovenia is geologically very heterogeneous. On its approx. 20.000 km^2 different types of bedrocks exist, thus reflecting in different $^{87}Sr/^{86}Sr$ signatures. As the underlying geological terrain changes, so will the isotope ratio of the strontium released from the rocks into the biosphere above. The aim of this study was: *i)* to optimise the Sr isolation method from the milk and *ii)* to investigate the potentiality and limits of using precise $^{87}Sr/^{86}Sr$ ratio measurements, determined by multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS), to discriminate Slovenian milks of different geographical origins. Additionally, we determined the $^{87}Sr/^{86}Sr$ isotope ratio of a candidate material (milk powder) as it has a similar matrix as milk samples. The determined value ($^{87}Sr/^{86}Sr$ = 0.70843 0.00009) was comparable with results obtained from 4 different laboratories participated in interlaboratory comparison.

Despite a complex matrix with high fat and low Sr content, the extraction chromatography was proved to be effective for Sr extraction from milk samples. The $^{87}Sr/^{86}Sr$ ratios measured in milk samples from different places in Slovenia showed that we are dealing with a complex lithological area. The results showed that the $^{87}Sr/^{86}Sr$ ratios of milk samples differ within a certain region. For example, milk samples from two locations with a distance of 16 km, namely Gornja Radgona ($^{87}Sr/^{86}Sr$ = 0.71199 0.00001) and Radenci ($^{87}Sr/^{86}Sr$ = 0.72481 0.00001), have different values. On the other hand, some milk samples from three different regions have a very similar isotopic composition (for example, Sevnica with $^{87}Sr/^{86}Sr$ ratio of 0.70925 0.00001, Vinica with $^{87}Sr/^{86}Sr$ ratio of 0.70948 0.00001 and Šmarje pri Jelšah with $^{87}Sr/^{86}Sr$ ratio of 0.70986 0.00001). This may be a result of diverse geology as well as a source of cow's diet (feed) which is not necessarily from the same region where cows graze. The determination of Slovenian milk provenance is a complex task that needs further investigation.

Keywords: stable isotopes, food provenance, strontium, MC-ICP-MS

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THP-9 Comparison of four mass spectrometric techniques for lithium isotopic measurements

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Lithium has important uses in nuclear power plant today and its isotopic composition must be determined at different stages of nuclear fuel cycle. Mass spectrometric techniques give the best performances in terms of precision and accuracy for lithium isotope ratio. The objective of this study is to compare the performances of four mass spectrometric techniques: thermal ionization mass spectrometry, multicollector inductively coupled plasma mass spectrometry, glow discharge mass spectrometry and quadrupole inductively coupled plasma mass spectrometry. Firstly, the study is based on pure lithium carbonate certified reference materials in order to develop and validate the analytical procedures. For each technique, inherent phenomena (mass bias or isotopic fractionation) were carefully corrected and the analytical performances were compared in terms of isobaric interferences, stability, accuracy and precision. Evaluation of uncertainties was carefully performed and the main uncertainty sources for each technique were identified. Secondly, specific analytical procedures were developed for more complex matrix samples, including dissolution and chemical purification. The chemical separation was performed by ion exchange chromatography in order to obtain a pure fraction of lithium. This procedure of purification was validated at each stage in order to prevent any isotopic fractionation during the separation and was applied to real samples with different isotopic composition. Furthermore elemental concentration on real samples was evaluated by isotope dilution technique. In the case of glow discharge mass spectrometry, isotope ratio measurements are directly performed on solid samples and precision and accuracy obtained were compared to the other mass spectrometric techniques.

Keywords: lithium isotope ratio, mass spectrometry, uncertainties

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THP-10 Bringing white into light: a multi-analytical approach studying lead-white pigments in paintings

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The art market nowadays is willing to pay exorbitant prices for paintings in the order of millions, but the verification of provenance for especially old paintings to prevent fraud can still be challenging **[1]**.

Additionally to classical art-historical research, modern analytical methods concerning the material characterization are of precious help to identify material anachronisms. In the rather traditional world of art conservation, the physical interaction with the objects should be kept to a minimum and therefore non-invasive measurements are the methods of choice even so they have their limitations. Any invasive sampling is avoided or has to have an obvious value in information.

The presented work will describe the chemical analysis of white carbonate-bearing pigments of paintings, specifically cerussite ($PbCO_3$) and hydrocerussite ($2PbCO_3{\cdot}Pb(OH)_2$), hereby combining the capabilities of radiocarbon dating for age determination while lead isotopes abundance ratios will be used to identify the place of origin.

Following technological advances in AMS, sample requirements for ^{14}C dating have been minimized allowing to sample artworks, in particular the paint layers itself and not only the support material **[2]**. The workflow consists of a multi-method approach including: a minimally invasive sampling of the pictorial layer in the mg range, XRF and FT-IR measurements with regards to the different chemical species of the sampled paint and 14C-age determinations by accelerated mass spectrometry (AMS) by degradation of the carbonate to CO2 with the aid of phosphoric acid **[3]**. The remaining sample is then digested, diluted and analysed for the elemental composition and for the isotopic composition of lead either by Q-ICP-MS and MC-ICP-MS **[4]**.

Several original paintings, dating from the 17th to 20th century, were analysed by our approach. Qualitative investigations by XRF and FTIR allowed to assess the presence of possible interferences (i.e. interfering additives) and preselect suitable samples for the ^{14}C-dating. The following ^{14}C-dating of the $PbCO_3$ provided an age for the carbon source of the carbonate and gave insight into the production processes of the white pigment. When produced from fermentation process as in the traditional stack process, the radiocarbon ages of lead white pigments match their production years and may also allow the dating of the painting **[3]**. Industrial processes however have a distinct depleted ^{14}C signal, which can be used as a marker to differentiate lead white produced with industrial methods from the traditional approach.

The quantification of the lead refers directly to the overall amount of all lead species and in combination with the carbon content could be used to determine the actual lead-white fraction in the sample. Furthermore, the isotope signatures of lead gave indications for the geographical location of the raw material sources with regards to European ores **[4]**.

This study proposes a novel complementary use of different techniques to assess age or production process and location information from a single sample of lead white paint.

Keywords: MC-ICP-MS, ^{14}C, multianalytical, lead

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THP-11 Elemental and isotopic analysis of serum from age-related macular degeneration patients by means of single-collector and multi-collector sector field ICP - mass spectrometry

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Age-related macular degeneration (DMAE) is a disease of the ageing eye and the leading cause of irreversible blindness among persons aged 65 years or older. At present, 60 million people are suffering from this ocular disease. DMAE proceeds without causing any pain to the patient and its diagnosis is based on the evaluation of characteristic signs, such as the progressive loss of visual acuity, difficulty with reading, and the presence of specific macular features.

It is known that both Cu and Zn play an essential role in the visual cycle, so a modification in their homeostasis can result in retinal disorders. This alteration in the homeostasis may be associated with changes in both element concentrations and isotope ratios. The main purpose of this work has been to study whether patients of DMAE show a systemic alteration of major and essential trace element concentrations at serum level. Also, Cu isotope ratios have been investigated. Control samples were obtained from a group of patients suffering from cataract.

Keywords: age related macular degeneration, elemental and isotopic analysis, multicollector ICP-MS, sector field ICP-MS

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THP-12 Direct determination of isotopic ratio of chromium species by HPLC–low resolution multicollector ICP-MS

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Chromium with different oxidation states exhibits significantly different behaviors in terms of potential toxic effects on environmental and biological system **[1]**. Cr(VI) is known as carcinogenic while Cr(III) is an essential element for the proper functioning of living organism. Because chromium is widely used in industrial activities such as electrical plating and chromium tanning, Cr(VI) could be easily released into the environment including surface water and groundwater, thus could pose a health risk. Therefore, environmental remediation is of interest. The commonly used approach is to reduce Cr(VI) which is highly toxic, mobile and bioavailable into Cr(III) which is in turns less toxic, immobile, and strongly adsorbs on solids' surfaces. Interestingly, the reduction of Cr(VI) to Cr(III) is often associated with an isotopic fractionation referring to the progressive change in isotope ratio $^{53}Cr/^{52}Cr$ of each individual chromium species. Thus, chromium stable isotopic ratios can be used as indicators to quantify the extent of Cr(VI) reduction in environmental remediation efforts **[2]**.

The aim of this work is to develop a method allowing for isotopic ratio measurements of chromium species present in a sample. This method is a combination of a liquid chromatography with a multicollector inductively coupled plasma mass spectrometry (MC- ICP-MS). The first task is to separate Cr(III) and Cr(VI) by using reversed phase ion pairing chromatography (RPIP- HPLC). During the separation, no interconversion between two chromium forms should be observed. The second task aims at isotopic ratio measurements by employing MC-ICP-MS. In this task, not only the isotopic ratio of $^{53}Cr/^{52}Cr$ but also $^{50}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ are studied in order to examine whether the measurement is correct. Because of a high degree of sample purification to avoid potential matrix effect as well as interferences is required for high precision determination of Cr isotope ratios in natural samples, the elimination of isobaric interferences from ^{50}Ti, ^{50}V on ^{50}Cr and ^{54}Fe on ^{54}Cr for chromium species is also investigated. This chromatographic separation together with desolvating nebulizer and on-line blank measurement gives a possibility of measuring chromium isotope ratio even in low resolution mode of mass spectrometer.

Keywords: chromium, Cr(III), Cr(VI), toxic, essential element, chromatography, MC-ICP-MS, isotopic ratio

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THP-13 Sr and Pb isotope ratio analyses and its application to investigate cultural interactions in ancient Nubia (2nd millennium BC)

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The "Across ancient borders and cultures"-project (FWF START Y615-G19) has investigated a settlement on Sai Island (Nile) in Upper Nubia (modern Sudan) as a part of the southwards directed Egyptian expansion in the New Kingdom (c. 1539-1077 BC). In the course of the investigations, novel analytical tools based on isotopic analysis were applied in order to gain new insights in the coexistence and merging of cultures in the 2nd Millennium BC of Egypt and Nubia.

Strontium (Sr) and lead (Pb) isotopes were applied for the analysis of skeletal remains and archaeological findings. Both isotopic systems have evolved into key tools in anthropology and archaeology for tracing residential changes and living conditions of ancient humans as well as trading and social interactions. The accurate determination of Sr and Pb isotope ratios by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) requires the separation of both analytes from the sample matrix (especially Ca) to avoid matrix-related effects (e.g. isobaric interferences, instability, mass fractionation effects and loss of sensitivity) from solutions containing

> 200 $g.g^{-1}$ Ca. An optimized separation method using DGA resin on the prep*FAST-MCTM* (Elemental Scientific, Omaha, USA) was applied in this study **[1]**.

The $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios of tooth enamel ("archive of childhoo") were investigated in order to identify Egyptian "colonialists" (non-autochthonous) or Nubian indigenes (autochthonous) as part of the ancient population of the Egyptian settlement on Sai Island. Nine human individuals were revealed as member of the autochthonous population of Sai Island even though they were buried in Egyptian style.

In case of naturally growing/present raw materials, the isotopic composition of the raw material (e.g. clay used for pottery) serves as indicator of the locally specific fingerprint. In the context of Sai Island, Nile mud, clay and ceramic pottery samples dating from the New Kingdom were analysed for their $n(^{87}Sr)/n(^{86}Sr)$ and $n(^{207}Pb)/n(^{206}Pb)$ isotope-amount ratios to investigate the possible differentiation between Egyptian style pottery imported to Sai Island and Egyptian style pottery produced on Sai Island.

Keywords: archaeometry, MC-ICP-MS, migration studies, New Kingdom, analyte/matrix separation

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THP-14 Trace of anthropogenic nitrate in groundwater by isotopic proxies in Kumamoto area, Japan

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Water is essential for the organism in the earth and its quality and quantity must be maintained for sustainable usage. In these last few decades, isotopic traces have been used to understand the origin and flow of groundwater. In this study, we analyzed various isotopes from groundwater samples in Kumamoto area, Japan.

Nitrate (NO_3^-) is one of the major anthropogenic contaminants in groundwater worldwide and a recent increasing trend is observed in Kumamoto area. Their origin is usually estimated from isotope ratios of nitrate ($^{15}N/^{14}N$ and $^{18}O/^{16}O$), but the denitrification process during the flow of groundwater changes the $^{15}N/^{14}N$ ratios. Here we tried to trace the nitrate input source using $^{11}B/^{10}B$ and $^{87}Sr/^{86}Sr$ ratios dissolved in water as well as concentrations of B, Sr and major dissolved ions. Boron is a conservative trace element in typical groundwater system according to the changes in pH, Eh and EC, and its isotope ratios have very wide variations (3%) in nature owing to its relatively large mass differences. Boron isotope ratios have been applied recently to groundwater studies owing to the multiple collector ICP-MS, because the major input sources of nitrate from mineral fertilizer and animal manure have different isotope ratios. Stagnant groundwater and thermal fluids tend to have low values and seawater has high values, so the isotope systematics is also useful to estimate the origin of groundwater.

Resultant hexa-diagram of major dissolved ions showed differences in groundwater quality between the northern area and the central and eastern areas, and the influence from seawater was observed in the coastal area (western areas). Data from the northern area had an enriched feature of NO_3^- as the anion and Ca as the cation. This indicated an anthropogenic input from mineral fertilizers. The analysis of B isotopic ratio, ^{11}B ranged from +3.1 to +30.9 permil, and some samples in the north and in the coast had high value in contrast to the low values in the central area. The $^{11}B/^{10}B$ trend was compared to a traditional isotopic tracer of $^{87}Sr/^{86}Sr$ ratios and the origin of nitrate will be estimated in the presentation.

Keywords: isotope ratio, groundwater, anthropogenic nitrate, tracer

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THP-15 Calibration of Mg isotope amount ratios and delta values

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In the past, $^{26}Mg/^{24}Mg$ measurements were referenced to NIST SRM 980, the initial zero of the $^{26}Mg/^{24}Mg$ scale. With the development of MC-ICP-MS, the detection of small but measurable isotopic differences in different chips of SRM 980 became apparent. To solve this problem, a suite of magnesium isotope reference materials, ERM-AE143, -AE144 and -AE145, has been certified in a first study by applying an ab initio calibration for absolute Mg isotope ratios without any *a priori* assumptions, a procedure which fulfils all requirements of a primary method of measurement. We could achieve for the first time measurement uncertainties for isotope amount ratios close to the typical precision of magnesium delta values, $^{26}Mg/^{24}Mg$, which are at the 0.1 ‰ level (2SD). In addition, it was demonstrated that commonly used fractionation laws are invalid for correcting Mg isotope ratios in multi-collector ICP-MS as they result in a bias which is not covered by its associated uncertainty. Depending on their type, fractionation, laws create a bias up to several per mil, with the exponential law showing the smallest bias between 0.1 ‰ to 0.7 ‰.

With these isotope reference materials, it is possible to establish SI-traceability for magnesium delta measurements. To realize this, we organized a second study within which five expert laboratories participated to cross-calibrate all available magnesium isotope standards, which are NIST SRM 980, IRMM-009, ERM-AE143, ERM-AE144, ERM-AE145 and the standards DSM3 and Cambridge-1. The mean $^{26}Mg/^{24}Mg$ values for the individual iRMs, calculated from the laboratory means show 2 SD reproducibilities varying between 0.025 and 0.093 ‰. Propagated measurement uncertainties suggest a standard uncertainty of about 0.1‰ for $^{26}Mg/^{24}Mg$ determinations (2SD). Thus, SI traceability for magnesium isotope amount ratios and delta values is demonstrated to be established.

Keywords: delta values, absolute isotope ratios, magnesium, isotope mixture approach

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THP-16 Stable isotope ratio analysis of Pb, S and Sr in plant-available element fractions: targeted sampling and on-site interferent separation by diffusive gradients in thin films (DGT)

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The measurement of stable isotope variations of Pb, S and Sr in complex environmental matrices such as soils and soil solutions remains an analytical challenge because spectral and non- spectral matrix interferents can substantially hamper accurate isotope ratio analysis by mass spectrometric techniques. The recent development and application of diffusive gradients in thin films (DGT) in stable isotope research opened up new opportunities for the targeted sampling of labile, plant-available fractions of multiple isotope systems in soil environments. The technique allows for simultaneous on-site speciation, analyte pre-concentration and matrix separation.

In this study, these major analytical assets of the DGT technique are combined with accurate determination of isotope amount ratios by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to assess the composition of stable sulfate-S, Pb and Sr isotopes in DGT-labile (*i.e.* reversibly adsorbed) soil element fractions. The aim of the work is to establish combined sulfate-S, Pb and Sr DGT sampling procedures in combination with MC-ICP-MS isotope ratio measurement. The developed techniques will be used to determine the isotopic composition of labile sulfate-S, Pb and Sr fractions in topsoils as georeferenced proxy for food provenance.

The study showed that DGT binding gels based on Amberlite IRA-400 anion exchange resin substantially improved $^{34}S/^{32}S$ MC-ICP-MS measurements in labile soil sulfate fractions by separation of S from major matrix elements (Na, K, Ca) during DGT sampling. The well- characterized Chelex-100 DGT technique shows a high potential to obtain the labile phase of Pb. Moreover, first results using a novel DGT technique for quantitative and selective sampling of labile Sr will be presented.

Keywords: diffusive gradients in thin films (DGT), MC,-ICP-MS, stable isotope ratio, soil biogeochemistry, food provenance

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THP-17 Submicrogram sulfur isotope analysis by EA- MC-ICP-MS

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Variations in the relative isotopic composition of sulfur provide critical insights into biogeochemical processes and sulfur isotope abundance determinations are fundamental to research in forensics, environmental monitoring and biochemical interactions. Often, the amount of material available for analysis is limited to a few micrograms or even sub-microgram quantities of the element. In this talk, we will describe the rather simple modifications made to a commercial elemental analyzer and the interface that was constructed to enable the high sensitivity analyses of sulfur. Isotope amount ratios $^{34}S/^{32}S$ and $^{33}S/^{32}S$ from microgram and submicrogram quantities of the element were determined in sulfide and sulfate materials using an elemental analyzer coupled to a ThermoFisher Scientific Neptune multiple collector inductively coupled plasma mass spectrometer. Operating in medium resolution mode, the sulfur isotopic composition of transient signals produced from the conversion of sulfur to SO_2 gas were referenced to pulses of SF_6 gas to assist with the correction of mass bias and calculation of $d^{34}S$and $d^{33}S$ values.

Keywords: sulfur, isotope, MC-ICP-MS, continuous flow

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THP-18 Hg isotopic measurements for atmospheric mercury at the Cape Hedo atmosphere and aerosol monitoring station (CHAAMS), Japan

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Mercury, Hg, is a globally spread pollutant, which exists in various chemical forms in the environmental systems. For better understanding of the Hg atmospheric cycling, it is important to characterize Hg emission sources, such as anthropogenic and natural, and link the sources to Hg exposure of the environmental system. Since the utility of Hg isotopic ratios in atmospheric mercury has been discussed to understand its source(s), we obtained Hg isotopic compositions of gaseous elemental mercury (GEM) collected at the Cape Hedo atmosphere and aerosol monitoring Station (CHAAMS), Japan. Our annual monitoring results showed a seasonal trend especially for ^{202}Hg values. We also observed clear positive correlations between ^{202}Hg values of GEM, and CO and PM2.5 concentrations in the summer. According to the meteorological data, the GEM might be derived from anthropogenic and/or natural sources, mainly from the southwest, and mixed with background air in the summer.

Keywords: Hg isotopes, GEM, CV, MC-ICP-MS, atmospheric mercury

α - Presenting author

THP-19 Analysis of anthropogenic Gd emissions into the German North Sea and potential new insights by the analysis of Gd isotope ratios in MRI contrast agents

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Gd-based magnetic resonance imaging (MRI) contrast agents have been widely used for medical applications over the last decades. Due to their highly hydrophilic chemical properties the Gd-based contrast agents are rapidly excreted without undergoing metabolic changes by patients after administration. Subsequently, waste water treatment plants (WWTPs) do not effectively remove Gd-based contrast agents, which allows them to enter the aquatic environment where no significant degradation is known to occur. Taken into account an amount of aprox. 1-3 g of chelated Gd per administration and several million MRI applications per year only in Germany, significant amounts of Gd enter the aquatic environment on a daily base. In order to characterize the anthropogenic Gd emissions caused by MRI contrast agents, recent studies dedicated to the calculation of anthropogenic Gd amounts have been presented. Furthermore, Gd speciation analysis opened further insights into the present species of Gd in the aquatic environment.

A new, potential analytical tool to better understand the chemical behavior of Gd in the environment lies in isotope ratio analysis via multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, only little is known about the natural terrestrial isotopic abundance variation of Gd. Furthermore, measurement procedures for accurate Gd isotope-amount ratio analysis need to be developed and validated to access the expected small variation.

This poster presents an overview of anthropogenic Gd emissions into the German North Sea and its catchment including the major tributaries (Elbe, Weser, Ems and Rhine). Herein, the anthropogenic Gd amounts were calculated based on the PAAS-normalized REE content of selected water samples. Based on this approach the majority of the analyzed samples were significantly influenced with anthropogenic Gd. In some cases, up-to 95% of the total Gd were of anthropogenic origin. Furthermore, first results from the Gd isotope-amount ratio analysis of certain commercially available MRI contrast agents (Dotarem™, Gadovist™, Omniscan™, Magnevist™, MultiHance™) after acid assisted digestion and analysis via MC-ICP-MS (NuPlasma II) are presented.

Keywords: MC-ICP-MS, Gd, MRI, environmental, North Sea

α - Presenting author

THP-20 On-line coupling of a liquid chromatograph to a multicollector ICP-MS for the direct measurement of Pb isotope ratios in samples of archaeological interest.

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Traditional MC-ICP-MS Pb isotope ratio measurements require an off-line tedious and time- consuming separation procedure using expensive chromatographic material. Moreover, sample availability, particularly for archaeological materials, can be sometimes limited and that can reduce the accuracy and precision of Pb isotope ratio measurements. For all these reasons we have developed an on-line chromatographic method to perform the separation of Pb from possible interferences and to measure directly the Pb isotope ratios on the digested full sample.

The HPLC chromatographic procedure selected was anion exchange and the different elements were separated as their anionic EDTA complexes. Chromatographic optimisation was performed injecting standards of different metals (Fe, Zn, As, Sn, Pb and Cu), prepared in 100 mM EDTA. Different mobile phases were checked in a Q-ICP-MS, and the best separation was achieved with a 25 mM ammonium nitrate-5 mM EDTA mobile phase, allowing the complete separation of lead from the rest of the metals in less than 10 minutes.

By coupling the HPLC system to the MC-ICP-MS we have evaluated different integration times and different Pb concentration levels using NIST SRM 981. Isotope ratio measurements were performed using the Linear Regression Slope (LRS) procedure using Tl added post-column as internal standard. The results obtained have shown that there was no isotopic fractionation during the separation process regardless the Pb concentration level. The lowest uncertainty was obtained for the shortest integration time of 0.13 s.

Keywords: lead, isotope ratios, HPLC, MC, ICP, MS

α - Presenting author

THP-21 Past environmental pollution in an industrial site: using stable lead isotopic analysis to identify multiple contamination sources.

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The reconstruction of the pollution's history that affects contaminated sites is a key point in environmental remediation. It is fundamental to recognize and characterize all the pollution sources involved, in order to estimate the extent of the damage and define the areas that need specifics remediation treatments. The identification of lead pollution sources is a difficult task in a typical industrial setting because of the large number of possible sources such as direct emissions from industrial sites, inappropriate waste disposal, exhaust from fuel combustion or spills, leaded pesticides and, obviously, the natural geological background.

The historical analysis of the areas based on information retrieved from the local authorities, can be a good starting point, but sometimes the lack of archived data can lead to a wrong estimation of pollution sources and consequently of the contamination's entity. Isotopic measurement tools combined with the concentrations mapping of the site, can overcome this problem, and allow to establish the true extent of the contamination. In particular, the fingerprint of an element given by its isotopic composition can be used to track the sources and transport pathways of heavy metals in pollution studies. Moreover, it is also possible to evaluate the relative contribution of the major pollution sources and determine if other point or non-point sources are present.

In the proposed case study, it is showed the initial monitoring activity of a lead- contaminated industrial site in Bagnolo Mella (Italy), active from 1897 to 1999. This site is going to undergo a future remediation action. From the analysis of various historical documents, this area was subjected to a heavy lead pollution (ca. 1858 mg/Kg dw of Pb) probably originated from the "lead chambers process" used in the production of sulfuric acid. The isotopic pattern of four different samples taken in this area, showed clearly that the lead pollution cannot be attributed only to sulfuric acid production, but also to other sources such as fuel spill or non-point sources.

Keywords: enviromental remediation, Lead, Pb, Stable isotope analysis, Heavy metal pollution

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THP-22 Determination OF 236U/238U ratios in environmental samples using ICP-MS/MS.

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Because of the virtual absence of 236U in the environment and its abundance closely related to its provenance, the 236U/238U ratio has been commonly employed as a tracer to provide information on source identification for safeguard purposes, nuclear forensic studies and environmental monitoring.

Due to their high-performance capabilities, ICP-MS techniques are currently the most widely employed to perform radionuclide determination. However, in the case of 236U and due to its very low relative abundance, its determination is limited by the formation of 235U1H+ in the plasma and by the influence of the tail of the major isotope 238U (abundance sensitivity).

In this work, we present an approach based on the ICP-MS/MS technology to determine 236U/238U ratios in environmental samples. The combination of two quadrupole-based mass filters, before (Q1) and after (Q2) the cell in the MS/MS configuration, provides abundance sensitivity values lower than 10-10, avoiding the influence of the 238U tail. In order to reduce the influence of the hydride–based interferences, desolvation systems have been employed in combination with mass-shift mode detection (Q1: U+ –> Q2: UO+). Best conditions provided a hydride rate value (235U16O1H+/235U16O+) in the order of 10-7. Finally, the methodology was validated with IRMM certified standards and successfully applied to the determination of 236U/238U ratios in environmental samples corresponding to sediments originating from the radioactive contamination plume caused by the Fukushima Daiichi Nuclear Power Plant accident. Ratios down to 10-9 have been obtained with precisions lower than 20%.

Keywords: ICP, MS/MS, uranium, 236, isotope analysis, Fukushima

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THP-23 Submicrogram sulfur isotope analysis by EA- MC-ICP-MS

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Variations in the relative isotopic composition of sulfur provide substantial insights into biogeochemical processes. Sulfur isotope abundance determinations have become fundamental to research in e.g. forensics, environmental monitoring, and biochemical interactions. Often, the amount of material available for analysis is fairly limited to a few micrograms or even sub- microgram quantities of the element. In this contribution we will describe modifications made to a commercial Elemental Analyzer and the interface to a multiple collector ICP-MS that was constructed to enable sulfur isotope amount ratios 34-S/32-S and 33-S/32-S from microgram and submicrogram quantities sulfur in sulfide and sulfate materials. The elemental analyzer was coupled to a ThermoFisher Scientific Neptune multiple collector inductively coupled plasma mass spectrometer. Operating in medium resolution mode, the sulfur isotopic composition of transient signals produced from the conversion of sulfur to SO2 gas were referenced to pulses of SF6 gas to allow for the correction of instrumental isotopic fractionation and calculation of DELTA_34/32S_IAEA S1 and DELTA-33/32S_IAEA S1 values.

Keywords: sulfur isotopes, MC ICP, MS

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THP-24 Comparison of different mass bias correction procedures for the measurement of Hg species-specific isotope ratios by Gas Chromatography coupled to multicollector ICP-MS

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Mercury is a global pollutant released to the atmosphere by natural and anthropogenic processes, and occurs in different chemical forms and/or oxidation states in terrestrial, atmospheric and aquatic ecosystems. On one hand, the determination of the different Hg species in a sample (speciation analysis) can be very helpful to understand Hg biogeochemical cycle as Hg reactivity, mobility and bioaccumulation depend on its chemical form. On the other hand, the accurate and precise measurement of Hg isotopic composition in real samples is a valuable tool to understand Hg pathway in the environment and to fingerprint contamination sources. Therefore, the coupling of chromatographic techniques to multicollector instruments to measure compound-specific Hg isotopic compositions may lead to new insights into the biogeochemical behavior of mercury species in the environment.

Optimum GC separations provide very short transient signals (typically 2-5 s at the peak base). Therefore, the number of acquisition points during the chromatographic peak is not enough to obtain comparable levels of accuracy and precision in the isotope ratio measurements than those obtained when measuring continuous signals. The accuracy and precision of compound-specific isotope ratios was improved by calculating the isotopic ratios from the slope of a linear regression between isotopic signals. This strategy was initially developed by Fietzke et al [1] for transient signals obtained by Laser Ablation coupled to MC-ICP-MS and lately applied by Epov et al [2].

When calculating delta values GC-adapted standard-sample-standard bracketing approaches have been shown to provide external reproducibilities lower than 0.5 ‰ [2] expressed as 2SD. The standard-sample-standard bracketing approach corrects for most of the mass discrimination effects but the elution of the sample matrix from the GC column may induce plasma instabilities affecting mass bias during the chromatographic peak profile of Hg compounds. Mass bias correction is typically carried out with the measurement of the 205Tl/203Tl isotope ratio in a nebulised Tl solution mixed with the Ar flow transporting the eluted Hg compounds from the GC column. However, the data treatment for mass bias correction when measuring compound-specific isotope ratios from the slope of a linear regression between isotopic signals has not been deeply investigated yet. This work reports the effect of different mass bias correction procedures on the accuracy and precision of Hg(II)-specific isotope ratios by GC-MC-ICP-MS.

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Keywords: GC, MC, ICP, MS, Mercury, Mass bias

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THP-25 IUPAC Commission on Isotopic Abundances and Atomic Weights - CIAAW

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The year 2019 marks the 100th anniversary of IUPAC and also the 150th anniversary of the development of the Periodic Law of the Elements independently by Dmitri Mendeleev and Lothar Meyer.

The Commission on Isotopic Abundances and Atomic Weights (CIAAW) is an international scientific committee of the International Union of Pure and Applied Chemistry (IUPAC) under its Inorganic Chemistry Division and entrusted with periodic critical evaluation of atomic weights of elements. Formally established in 1899, the Commission on Isotopic Abundances and Atomic Weights remains one of the oldest continuously serving scientific bodies. It was created to introduce uniformity in the atomic-weight values used worldwide.

Since the 1970s, CIAAW evaluates other cognate data, such as the isotopic composition of elements.

Members of the Commission meet biennially where matters pertaining to the Commission's purview are discussed. The biennial CIAAW Standard Atomic Weights serve as primary source for Atomic Weight values worldwide for science, trade and also educational purposes.The tables serve as the authoritative source in science and appear worldwide on the periodic table wall charts. Several subcommittees of CIAAW are entrusted with related topics such as isotopic abundance measurements, stable isotope reference material assessment and the natural assessment of fundamental understanding of isotopes.

Besides the Table of Standard Atomic Weights, the Commission publishes a variety of documents: Atomic Weight reports, isotopic composition reports, element-by-element reviews, technical and educational publications.

In this poster the Commission, key tasks and functions as well as current projects related to the mass spectrometry community are presented. All documents are also available on the CIAAW webpage (www.ciaaw.org) along with further information about commission-related topics.

Keywords: IUPAC, periodic table of the elements, atomic weight, CIAAW

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THP-26 The role of single particle ICP-MS with microsecond time resolution in a multi-technique approach for unveiling the biological fate of ingested nanoparticles

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In the food sector, applications of nanotechnologies to agricultural production, food processing, and food contact materials are rapidly developing. Nanotechnology applications in the food sector may bring benefits; on the other hand, potential risks have to be assessed and excluded. Relevant information for performing an appropriate nano-specific risk assessment is also required for a number of currently used food additives and nutrient sources in particulate form, which are not nanotechnology products but present a substantial fraction of nano-sized particles.

The recent EFSA Guidance for nano-specific risk assessment set out a framework for step- wise hazard identification and characterisation **[1]**. The first step investigates whether the nanomaterial undergoes a quick degradation (e.g. dissolution) under conditions representative of the gastrointestinal tract, thus losing the nanoparticulate nature. Nanomaterials that quickly dissolve/degrade in the gastrointestinal tract do not give rise to nano-specific concerns and standard risk assessment can be followed. Only if nanoparticles persist as such after gastrointestinal digestion they may be absorbed in the gut. In this case, it is necessary to investigate their stability of under lysosomal conditions to assess the potential for intracellular accumulation.

Within the NANOPERSIST project, the time-dependent transformations of nanoparticles under conditions representative of the gastrointestinal tract and lysosomes have been studied by robust in vitro methods with standardised protocols complying with the guidance **[1]**. A state-of-the- art multi-technique approach (transmission electron microscopy, single particle ICP-MS, AF4-UV- MALS-ICP-MS/MS, centrifugal liquid sedimentation, dynamic light scattering) has been used for the physicochemical characterization of the particles in pristine conditions, after ingestion in fed and fasted conditions, and after lysosomal processing. Ten different materials belonging to four chemical classes (synthetic amorphous silica, titanium dioxide, iron oxides/hydroxides, and zinc oxide) were studied. TEM was essential to study particle morphology and primary size. DLS and CLS gave an insight about the agglomeration behaviour of the pristine material at different pH conditions. However, only spICP-MS with the use of µs dwell times combined with ion–molecule chemistry for resolution of spectral interferences enabled to obtain quantitative data on the mass concentration and number-based distributions in biological simulated fluids for most material types.

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THP-27 "Not your kid's apple juice": an examination of arsenic content in american and european hard ciders

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Alcoholic hard ciders have a long history around the world but only have become readily available in the United States over the past decades. Recent studies have been conducted showing the presence of arsenic in apple juices and wine. Arsenic based pesticides, particularly lead arsenate, were in widespread and use in the United States up until the final ban in 1988. Despite arsenic residue being recognized as a potential problem from the turn of the century, lead arsenate was one of the most widely used pesticides in the nation and was applied to millions of acres of crops through the 1940's. Lead arsenate was the most commonly applied pesticide in apple orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, samples were obtained of popular American and European hard ciders. Modern hard ciders are produced from either fresh apples or apple concentrates. Samples were digested using microwave digestion and testing by ICP-MS and LC-ICP-MS to determine total arsenic content and potential content of different arsenic species.

Keywords: heavy metals, speciation, arsenic, beverage

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THP-28 Trace elements bioaccumulation and As biotransformation in sponges: uses of ICP-MS methodologies

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Urban development and anthropogenic activities affect coastal marine ecosystems worldwide. In particular, trace elements (TEs) originating from both natural and contaminated sources, leach into the marine environment by various ways. Monitoring the TE levels and their ecological impacts therefore constitutes an urgent topic. Marine organisms have been the focus of most studies related with TE monitoring due to the analytical issues linked to the treatment of seawater samples and also to the lack of sediments in some areas (i.e. in rocky shores). Widely distributed in coastal areas especially along the Mediterranean shoreline, sponges have been considered as potential bio-monitors of TE in the marine environment. Indeed, those sessile filter feeders have shown a great ability in accumulating TE. We will present the method development and optimization (ICP-MS and HPLC-ICP-MS) for the analysis of total TE content and As speciation in sponges. The bioaccumulation of TE will be then presented for six sponge species collected in the French Mediterranean and along the Irish coast, at sites of diverse anthropogenic pressure. This study revealed that both the sponge species and the availability of the TEs in seawater drive the bioaccumulation pattern. A high bioaccumulation factor was measured for Ag, As, Cd, Cu, Mo, Zn, underlying the potential of sponges as biomonitors for TE pollution. A "sponge watch program" may therefore offer an alternative to the widely used "mussel watch program". Specifically, the speciation of arsenic was investigated, because of its already documented bioaccumulation in sponges as well as to its high toxicity. Toxic inorganic As species (arsenate As(V)) were predominantly detected in seawater, whereas sponges were demonstrated to contain the predominant organic As specie: arsenobetaine (AsB). The potential of sponges for bio-transforming As was highlighted, supporting their use as potential bioremediation organisms in the field. With the aim to investigate the pathway of the conversion of As(V) from seawater into AsB in sponges, experiences in controlled conditions were undertaken. Specimens of the Mediterranean sponge *Haliclona fulva* were collected and maintained in running-seawater tanks. Following a 10 days-acclimation period, a group of specimens was kept in running-seawater tanks and a second group was transferred in running-arsenate-spiked-seawater tanks. Sponge specimens were further analyzed at different times during a 3-weeks incubation. The results showed similar As concentrations in sponges from uncontaminated or contaminated aquarium, but higher AsB concentrations in sponges living in the arsenate-contaminated aquarium. The higher concentration in AsB may result from the biotransformation of the added As. We therefore evidence a biotransformation of arsenic species by the sponge *H. fulva* and/or its microbial symbionts.

Keywords: trace element, arsenic, sponge, speciation, bioaccumulation, biotransformation

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THP-29 The fascinating world of arsenic speciation in mushrooms

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The arsenic speciation in mushrooms is, compared to other terrestrial and marine samples, very diverse and varies immensely between the different fungal species. Besides simple arsenic compounds like inorganic arsenic, methylarsonic acid or dimethylarsinic acid (which are the main compounds of terrestrial plants and animals), mushrooms can also contain high concentrations of "marine" arsenic species like arsenobetaine. The reasons for the occurrence of different arsenic species in different mushrooms are still unknown. Until now, the only known determining factor is the fungal species.

We investigated the arsenic species of aqueous extracts of all kinds of mushrooms, from typical edible mushrooms like *Boletus edulis* (porcini) to truffles and more unusually looking fungi like *Ramaria spp.* (coral mushrooms), with HPLC coupled to ICP-MS. Typically, anion- and also cation-exchange chromatography were employed for the separation of the different arsenic species. Molecular mass spectrometry was used additionally for the investigation of unknown compounds.

The presentation will cover various interesting new findings of the project. Special emphasis will be given to the detection of unusual arsenic compounds, for example dimethylarsinoylacetate or trimethylarsoniopropanoate. The discovery of a new arsenic compound, homoarsenocholine, for the first time in nature will also be presented. Our findings are important contributions for the elucidation of the transformation processes of arsenic in the terrestrial environment.

Keywords: arsenic species, speciation analysis, mushrooms, fungi

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THP-30 The use of ICP-MS for the characterization of seleno-compounds in bio-stimulated selected tomato varieties

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The aim of the project was to evaluate the process of bio-stimulation of various plants with selenium compounds and to characterize the metabolism of selenium by ICP-MS and HPLC-ICP- MS. The bio stimulation process was conducted towards increasing the nutrition value of vegetables, with the example of the selected tomato varieties. The project was conducted under the largest food-related initiatives worldwide, EIT food pan-European partnership, with a consumer- centered approach, to empower innovators, entrepreneurs and students to develop world-class solutions to societal challenges, accelerate innovation, create jobs and increase Europe's competitiveness.

The procedure for enriched tomato with various biologically active substances, produced in- situ by growing plants enriched with carefully selected bio-stimulants were developed firstly under laboratory scale conditions, that after proof-of-concept approach, was transfer to be used in field conditions. In between others bio-stimulants, selenium inorganic salts were selected to be added to the nutrient solution as it is known that various plants exhibit the potential to metabolize inorganic selenium ions into their organic derivatives. Those derivatives, namely seleno-aminoacids are essential in human, as they are considered as an essential nutrient for living organisms, of great importance for the proper functioning of the human organism with multiple biological activities, which depends on the content of selenium as well as nature of the seleno-compounds. The ICP-MS was used in order to evaluate the content of selenium in various plant tissues, including tomato used for the production of tomato juice towards understanding the efficiency of uptake and transportation of selenium in plants. Then HPLC-ICP-MS was used for the evaluation of the speciation of selenium in various plant's tissues towards understanding the bio-metabolisms of inorganic compounds of selenium used in nutrient solution.

Keywords: selenium, food

Acknowledgements

The project was financed by the project "Increasing nutritional value (bio-stimulated) of selected performant tomato varieties to be cultivated in areas with temperate climate" founded by European Institute of Innovation and Technology (EIT), under EIT Food pan-European partnership (2017-2018).

The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy (2007-2013).

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THP-31 Hyphenated techniques for the characterisation and application of metal labelled antibodies

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The use of metal labelled antibodies for immunohistochemical methods has expanded the possibilities of ICP-MS in biological applications beyond the sole investigation of the metallome, expanding the utility of ICP-MS for protein analyses in biological liquids or thin tissue sections. Quantification of proteins using metal labelled antibodies requires careful consideration of procedures to ensure that the integrity of the antibodies remain after the labelling step, the tagging efficiency and reproducibility, the stoichiometry of the antibody-antigen binding, as well as sensitivity and selectivity. In this work, we present novel methods for the application of hyphenated-ICP-MS as an integrated, robust and rapid tool for the characterisation of metal labelled antibodies for immunohistochemical applications. We also describe novel isotope dilution techniques and ICP-MS tune modes for LC-ICP-MS and LA-ICP-MS for robust quantification of proteins in biological matrices.

Keywords: ICP-MS, immunoassay, liquid chromatography, laser ablation

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THP-32 Provision of calibration services to underpine selenium speciation measurements in the clinic: results from a phase I trial of selenium in cancer patients

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Selenium (Se), an essential trace element, is commonly taken as supplement for the prevention or control of cancer due to its antioxidant properties. Randomized controlled trials of Se supplementation for cancer prevention have yielded conflicting results, pointing out the complexity of Se metabolism due to the different toxicological and physiological properties of Se drugs. Although small Se metabolites have been suggested to be most important mediating species in cancer prevention and treatment **[1]**, the role of selenoproteins such as selenoprotein P (SEPP1) as key biomarkers has been increasingly recognised not only for cancer but also for other critical diseases including Diabetes and Alzheimer's **[2]**. However, no Se speciation data has been reported so far for most undertaken trials, leaving out invaluable information to reach a better understanding of the observed effects. This is probably due to the lack of validated and straightforward methods that can be easily applied to obtain multi-species information in a large number of clinical samples.

For clinical purposes selenoproteins and, more in particular SEPP1, have usually been characterized and quantified using antibody-based enzyme immunoassays such as ELISA. However, those assays often suffer from a lack in selectivity, they are isoform-specific and results are usually associated with large measurement errors. Therefore, reference methods to determine SEPP1 in clinical samples **[3,4]**, are invaluable to help elucidate the bias of results from immunoassays and to validate more routine speciation methods.

This work will show the potential of ICP-MS, alone and/or in conjunction with liquid chromatography (LC), for the quantification of Se and Se-species in cancer patients samples from a *Phase I* clinical trial study of Se. This clinical research study aims to know the most effective and safer form of Se (Se-methylselenocysteine, L-selenomethionine and sodium selenite) in patients with either metastatic prostate cancer or chronic lymphocytic leukaemia. A systematic Se study was conducted in plasma patient samples collected before (baseline) and after 4 weeks of Se treatment. In order to assess a complete Se status, total Se measurements were performed along with speciation approaches for the determination of high and low molecular weight Se species, such as SEPP1 and selenomethionine (SeMet), respectively. The work will address the relevance of clinical speciation data to the understanding of the anti-cancer effects of dietary Se compounds for future clinical trials.

Keywords: calibration strategies to support clinical selenium measurements

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THP-33 Towards high throughput in speciation monitoring

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Arsenic, chromium and selenium are some of the key analytes which are evaluated for their presence and abundance in food due to their toxic or beneficial nature. Since the true answer to whether the analyte is harmless, harmful or useful lies within its chemical species, speciation evaluations are becoming increasingly common in food regulations.

Consequently, an increasing number of food safety assessments which require the speciation of analytes use LC-ICP-MS as their instrument of choice. This is because LC-ICP-MS allows the coupling of a chromatographic separation technique which is able to separate different chemical species of an element, with the low-level, isotopic detection capabilities of ICP-MS.

As the demand for food speciation applications grow, so does the need for the routine monitoring of such matrices, calling for reliable hardware and robust applications. In such settings, methods should be characterized by short run times, improving sample throughput and lowering the cost of analyses.

In this talk, we will present methods relating to the fast and efficient analysis of As, Cr and Se speciation in food matrices. Both ion-exchange and ion-pairing methods have been developed and are discussed in terms of their detection limits, accuracy, repeatability and suitability for the routine monitoring of food.

Keywords: speciation, food, LC-ICP-MS

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THP-34 Identification of cobalamin analogues in canine and equine urine via LC-MS-MS

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In recent years cobalt has come to the forefront of horse and dog racing as a hypoxia mimetic. Cobalt is a naturally occurring micronutrient and key component in the formation of B12, a generalised term used for cobalamins. Essential in all eukaryotes, the B12 cofactor helps catalyse a wide range of metabolic pathways, including methyl transfers, isomerisation, dehalogenation and ribonucleotide reduction (Giedyk et al, 2015, Karpowich et al, 2002, Santos et al, 2018). Cobalt has been shown to stabilise HIF1αleading to an increase of erythropoietin (EPO) production (Hoffmeister et al., 2017, Ho et al., 2015). Although the exact minimal dosage isn't clear, a recent cobalt chloride administration on humans showed that a 5mg oral dosage lead to an increase in EPO and 10 mg significantly increased plasma EPO levels (Hoffmeister et al., 2017). However, elevated levels of cobalt may cause necrosis and apoptosis in several cell lines raising concern about animal welfare.

In 2015 and 2016, following population studies, an international threshold of 100 ug/L cobalt in equine and canine urine was established in efforts to mitigate misuse of cobalt-containing supplements and cobalt salts as potential doping agents. Racing authorities and participants are currently interested in the identification of cobalt speciation to distinguish the use of cobalt salts from B12. Therefore, the racing industry is interested in implementing a quantitative method to distinguish cobalamin analogues and cobalt salts.

Analysis of Hydroxocobalamin (HOCbl), methylcobalamin (MetCbl), Coenzyme B12 and Cyanocobalamin (CNCbl) was performed by LC-ICP-MS. Canine and equine urine samples previously analysed via ICP-MS that yielded total cobalt levels at or above the threshold were analysed qualitatively to investigate the presence of cobalt analogues. Additionally, samples from intravenous administrations of veterinary pharmaceuticals known to contain CNCbl and cobalt salts that had previously been quantitatively analysed via ICP-MS were analysed via LC-ICP-MS for CNCbl.

LC-ICP-MS results show the presence of Co(II), HOCbl, MetCbl and CNCbl analogues in the canine and equine samples. As expected, Co(II) and CNCbl were present in the administration samples.

The analysis of cobalamin analogues in canine and equine urine may prove to be challenging due to the photosensitivity of B12 and potential analogue formations in urine due to upper ligand lability. Moving forward, analysis via LC-ICP-MS/MS is anticipated to facilitate a quantitative analysis for cobalamin analogues in canine and equine urine.

Keywords: cobalt, speciation, LC, MS/MS, ICP-MS, Cobalamin, B12

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THP-35 Experimental and analytical approaches to elucidate the role of phytoplankton in biotic and abiotic mercury (Hg) transformation

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Understanding of mercury (Hg) transformation pathways in the aquatic systems is an active research area. However, opposite to the extensive work on bacteria, the role of the phototrophic microorganisms in both abiotic and biotic transformations is not well understood. The determination of the kinetics and prevailing mechanisms of Hg biotic transformation pathways mediated by phytoplankton, on the one hand, and the examination of which and under which conditions biogenic ligands are produced by the phytoplankton are the main goals of this research. Gas and liquid chromatography coupled to ICP-MS and molecular mass spectrometry are used to get a significant progress in speciation analysis of Hg compounds and the elucidation of their binding ligands. Isotopically labelled Hg compounds are used to investigate simultaneous pathways at trace levels. Different experiments on both biotic and abiotic transformations mediated by phytoplankton have been performed and the preliminary results will be presented. This study represents the first stage of PHYTAMBA (Elucidating the role of PHYToplankton in Aquatic Mercury (Hg) Biotic and Abiotic transformations), an international and multidisciplinary research project, that involves a large range of areas including environmental and analytical chemistry, biochemistry and ecotoxicology.

Keywords: mercury, phytoplankton, abiotic/biotic transformation, aquatic systems, biogenic ligands

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THP-36 Ultratrace analysis of germanium species in natural waters by cryotrapping with ICP-MS and ICP- MS/MS detection

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Germanium is an element among so called technologically critical elements, quite rare in nature, but increasingly used and vital for modern technologies needed for modern communication, computing or the production of clean energy. Increased use also brings increasing demand for analytical methods for accurate Ge determination and speciation analysis at ultratrace levels in environmental samples. Inorganic Ge levels in unpolluted natural waters are in single or low tens of pg.L^{-1} for freshwater and in low pg.L^{-1} range in seawater, and methylated germanium species are below pg.L^{-1} in freshwater and up to 20 pg.L^{-1} in seawater. Analysis at those levels still pose a considerable challenge. Most of the published data have been obtained by hydride generation (HG) coupled to cryotrapping (CT) and either graphite furnace- AAS and recently also ICP-MS detection. With the fast progress of analytical methodology such as reaction cell ICP-MS and especially ICP- MS/MS technology, the analytical procedures need to be revisited for accurate analysis.

A semi-automated HG-CT-ICP-MS system, originally developed for arsenic speciation analysis **[1],** was adopted for Ge speciation analysis. HG conditions for individual species, with L- cysteine as reaction modifier, were optimized and compromise conditions found. Limits of detection below 0.1 pg.L^{-1} for all species were achieved. Results for river water reference material SLRS-4 agree well with so far published values; also SLRS-6 and seawater reference materials NASS-7 and CASS-6 were analyzed.

Pilot experiments of HG-CT with ICP-MS/MS detector will be presented.

Keywords: germanium speciation, volatile species generation, cryotrapping, ICP-MS

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THP-37 Investigation of transition metal species in lithium ion battery electrolytes by means of CE-ICP-MS – a new approach to reveal the dissolution mechanism of transition metals from cathode materials

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Lithium transition metal oxides containing iron, manganese, cobalt or nickel are commonly used as cathode materials in Lithium Ion Batteries (LIBs). Dissolution of these transition metals from the cathode, especially excessive manganese dissolution, can have strong negative effects on battery lifetime **[1]**.

There are several mechanisms described in the literature, which are responsible for transition metal dissolution: (1) material defects, (2) lattice stress resulting from lithium insertion and de-insertion, (3) acidic corrosion and (4) disproportionation of Mn^{3+} in the structure to soluble Mn^{2+} and solid Mn^{4+} **[2][3]**. Based on these proposed mechanisms, most studies claimed that the dissolved transition metals are present in oxidation state of +2. However, new studies suggested, that the formation of higher valances like Mn^{3+} could not be ruled out.

In few studies, the oxidation states of dissolved manganese in electrolytes were investigated for the spinels lithium nickel manganese oxide (LNMO) and lithium manganese oxide (LMO). In 2015, Jarry *et al.* identified soluble Mn^{3+} complexes on the surface of LNMO particles **[4]**. In a study from 2016, the amounts of Mn^{2+} and Mn^{3+} in electrolytes were investigated **[5]**.

These studies show that the dissolution behavior of transition metals might not be fully understood and needs further investigation concerning the dissolved transition metal species.

Quantification of labile Mn^{3+} is challenging due to favored disproportionation reaction of Mn^{3+} to Mn^{2+} and Mn^{4+} and because of its high redox potential.

In this work, a CE-ICP-MS method for simultaneously identification and quantification of soluble $Mn^{2+}$and Mn^{3+} amongst other transition metals was developed. To achieve separation of both manganese species, diphosphate was used as an auxiliary ligand in CE running buffer. It has the highest ability to stabilize Mn^{3+} regarding the preferred disproportionation reaction and is stable against the high redox potential of Mn^{3+}.

Different dissolution experiments with LNMO-based cathodes were performed and the recovered electrolytes were investigated afterwards regarding the dissolved manganese species. Additionally, the applicability of this method regarding the separation of Co^{2+}/ Co^{3+} and Fe^{2+}/Fe^{3+} was investigated.

Keywords: lithium ion batteries, transition metal speciation, capillary electrophoresis, ICP-MS

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THP-38 Studies on the influence of metal ions on maize (Zea mays) using LA-ICP-MS and ESI-MS/MS

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Elements taken up by plants can be divided into: indispensable for the proper functioning of the plant cell or unnecessary - not involved in cellular metabolism and toxic even in small quantities. Essential elements also induce toxicity symptoms if they are present in excess. Plants have homeostatic mechanisms that allow them to maintain correct levels of essential metal ions in cellular compartments and minimize the destructive effects resulting of their high content. The excess of metal ions taken up by plants is one of the main abiotic stress factors caused by physiological and biochemical changes. Plants developed various phytochemical defense mechanisms to cope with these stressful abiotic conditions. In addition to antioxidant systems (low- molecular antioxidants and specific enzymes), plants also produce flavonoids, phenylpropanoids or phenolic acids that can potentially serve as effective antioxidants. In response to stress, phenolic compounds can behave like metal chelators and can, on the other hand, directly remove reactive oxygen species.

The aim of the conducted research was to study the influence of metals such as Cd, Ni, Pb and Zn on phytochemical defense mechanisms of maize (*Zea mays*). For this purpose, two techniques has been employed to study on the phytochemical behavior of maize plants during exposure to higher concentrations of elements. Laser ablation with inductively coupled plasma mass spectrometry (LA-ICP-MS) follow the transport paths of selected elements in the tissues of maize. The developed procedure of mapping of the elements in thin section of maize tissues, i.e. root, stem and leaf allowed to indicate places of accumulation and possible path of migration elements in plant tissues. However, in order to identify the compounds produced by plants in response to stress a high resolution mass spectrometer Q-Exactive Orbitrap with a electrospray source (ESI-MS/MS) has been applied. Use of ESI-MS/MS allowed for confirming the presence of certain organic compounds. Phytochelatins (reduced and oxidized forms of peptides) and flavonoids were observed in roots, stems and leaves. Phytochelatins are bioindicators of stress and flavonoids are classified as low-antioxidants, which are important in the indirect inactivation of reactive oxygen species, but also as funcional food components. The validation of the analytical procedures confirmed that the procedures provide reliable results.

Keywords: elements, plant tissues, mapping, metallomics, phytochelatins, flavonoids, maize, mass spectrometry, LA-ICP-MS, ESI-MS/MS

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THP-39 Determination of the geographic origin of spices using elemental analysis after microwave digestion

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Competitive advantage within the food industry has lead to fraudulent activities like intentional counterfeiting, substitution, adulteration or mislabeling/misrepresentation of their ingredients. Many of these tricks go unnoticed by consumers and regulating government agencies due in part to the lack of standardized methods for identification. This highly specialized problem results in inferior products entering the marketplace and skewing price points for legitimate goods. For origin-driven products like spices, food fraud has highlighted the need for a way to defend claims of geographic origin. One good example of this is Madagascar vanilla, price per kilo has vaulted from €42 in 2012/13 to €340 in 2016/17, this leads to potential counterfeiting, substitution, etc. from bad actors in the food industry. This study uses three different technologies; microwave digestion, ICP-OES and ICP-MS, to determine if spice origin from different countries could be accurately distinguished. Spice samples were sourced from a large US importer of spices that can verify the country of origin. The results of this study demonstrate the validity and applicability of the analytical approaches used.

Keywords: spices, geographic origin, microwave digestion, ICP-OES, ICP-MS, elemental analysis

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THP-40 Maternal dietary habits, levels of selected elements and fatty acids composition in human milk from coastal and inland areas of Slovenia

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Human milk is considered as an essential and the best nutrition for healthy new-borns. Maternal diet and lifestyle can be associated with the levels of elements, composition of fatty acids (FAs) and stable carbon isotopes of FAs (*d*13CFA) in human milk, therefore we investigated whether these parameters could be used as indicators for dietary habits, particularly frequency of seafood intake.

Levels of selected toxic and potentially toxic elements were analysed using an inductively coupled plasma mass spectrometry (ICP-MS) for As, Cd, Cu, Mn, Pb, Se and Zn for milk samples and cold vapour atomic absorption spectrometry (CV-AAS) for Hg in milk. Identification and quantification of FAs in maternal milk were performed by in-situ trans-esterification method (FAMEs). The characterization of FAMEs were performed by gas chromatography with FID detector (GC-FID), equipped with a capillary column (Omegawax 320), while *d*13CFA were determined using gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) coupled to an IsoPrime GV IRMS, using a capillary column DB-1MS.

Questionnaire data and elemental and FAs composition of milk samples (4-6 weeks postpartum) of 74 women (20-38 years) from the coastal area of Koper (KP) and inland area of Pomurje (MS) from the national human biomonitoring in Slovenia (2007-2015) were used in data analysis. In addition to basic statistical analyses, data mining approaches for supervised (*i.e.* classification) and unsupervised (*i.e.* clustering) learning were applied to identify the geographical origin and the fresh seafood intake.

Results revealed higher levels of As and Hg in human milk in KP that could be related to fresh seafood intake. In order to distinguish between different levels of fresh seafood intake, our study demonstrated that % of specific FAs (iC17:0, C4, C18:2w6t, aC17:0, CLA and C22:4w6) and *d*13C of C18:1w9c in human milk could be used as appropriate indicators. Indeed, 71% of FAs and 30% of their *d*13CFA in milk differed statistically significantly between KP and MS indicating different feeding habits.

Keywords: fatty acids, carbon isotopes, human milk, ICP-MS, GC-C-IRMS, biomarkers, biomonitoring, data mining, food and nutrition

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THP-41 Tools for elemental speciation in clay - from CE-ICP-MS speciation to miniaturised clay column experiments using LC-ICP-MS

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The development of a high level nuclear waste (HLW) disposal in deep geological formations is a very important task for the future. The long term safety assessment for more than hundred thousand years needs a full knowledge of all processes of interaction between the radioactive waste and the surrounding host rock formations like claystone as natural barrier but also the interaction with the engineered barriers like cementitious materials as backfill and bentonites as buffer material **[1]**. A wide set of geochemical parameters can influence the retention of radionuclides originated from a leakage in a waste disposal for example competing ions released from the clay or cement concrete by infiltration of percolating water, natural organic matter (NOM) as complex forming ligands, changes in temperature or pH-milieu of the aquifer.

In this study, trivalent europium (homologue of americium) and uranium (VI) as main components of the HLW beside caesium and iodide were used and their interaction with clay or cementitious materials in the presence or absence of NOM was studied. To study the mobility of the analytes for example at high saline and hyperalkaline conditions (caused by the dissolution of clay and cement concrete in the presence of water), new analytical tools must be developed **[2]**. As speciation method, capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE-ICP-MS) was used to study the complexation behaviour of Eu(III) and U(VI) with NOM from different sources **[3]**. The influence of metal concentration, the presence of competing cations from clay or concrete dissolution as well as cations from clay porewater on the complexation behaviour were analysed. For the sorption/desorption studies, common batch experiments with the analytes and clay mineral suspensions are performed. Additionally, miniaturised clay column experiments (MCCE) with online ICP-MS coupling allow for the visualization of sorption and desorption processes of europium and uranium on clay dynamically. MCCE with compacted clay was used to study the influence of NOM on the metal mobility in clay like Kaolinite or Opalinus clay. LC hyphenation with ICP-MS leads to quantitative information on the elemental composition of the eluent from the clay column directly after determination of the UV/Vis-active compounds in the diode array detector of the LC.

Keywords: speciation, CE, LC, ICP-MS, uranium, europium, nuclear waste, clay, NOM

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THP-42 Boron isotope - amount ratio analysis via MC- ICP-MS in seawater and freshwater samples after micro-sublimation

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Boron has two stable isotopes, ^{10}B and ^{11}B, with isotopic abundances of 19.8 and 80.2 %, respectively, in naturally occurring terrestrial materials. The natural variability of the boron isotopic composition of naturally occurring terrestrial materials is about 80 ‰. Amongst other applications, B has evolved as promising tracer of different sources of water and mixing processes of *e.g.* freshwater and seawater because of the significantly different B isotopic composition, which depends on salinity, pH, pressure, ionic strength, etc.. Due to its versatile use in industries e.g. as sodium perborate as bleaching agent or as dopant for semiconductors, the boron isotopic signature may also be of interest as an anthropogenic tracer.

This contribution will address the potential of micro-sublimation as extraction and purification method for boron isotopic analysis in freshwater as well as seawater samples before their analysis via multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The complete method was optimized for low blank levels and low detection limits, high recoveries as well as a high reproducibility. Isotope ratio analysis were performed using a standard-sample bracketing approach, with NIST SRM 951a as accepted 0-anchor according to the IUPAC. The developed validated method was applied for the analysis of multiple water samples for boron concentration and boron isotopic composition of ($^{11}B/^{10}B$)SRM951a.

Finally, the potential of using B isotopes as anthropogenic tracer in the aquatic environment are explored by applying the validated method to selected samples from the German North Sea catchment including samples from the main tributaries Elbe, Weser, Ems and Rhine.

Beside characteristic mixing occurrences between freshwater and seawater signatures of ($^{11}B/^{10}B$)SRM951a ranging by > 40 ‰, small tributaries show characteristic signatures.

Keywords: boron isotopes, inductively coupled plasma mass spectrometry, waters, micro sublimation

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THP-43 Development of a LC-ICP-MS with a counter gradient method for quantification of decomposition products of lithium ion battery electrolytes

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Nowadays, lithium ion battery (LIB) electrolytes usually consist of organic linear and cyclic carbonates as well as the conducting salt $LiPF_6$. However, the electrolyte is thermally and chemically instable and, in presence of trace amounts of water, a huge variety of organo(fluoro)phosphates occur. The qualitative and quantitative analysis of LIB electrolyte decomposition products is not only relevant for understanding the aging mechanism but needs a view of potential toxic hazard. The formed organo(fluoro) phosphates are potential toxic with a similar effect mechanism to the chemical warfare agent sarin.

A reversed phase high performance liquid chromatography inductively coupled plasma mass spectrometry (RP-HPLC-ICP-MS) method was developed to characterize non-acidic organo(fluoro)phosphates. The formed decomposition products were separated by RP-HPLC with gradient elution.

Plasma fluctuations, which occur especially, during the change of organic content in the mobile phase, aggravate the quantification in the ICP-MS. To compensate these, two different approaches were used. With the first method, the phosphorus signal alteration was determined and the quantification was adjusted with a factor. For the second approach, a counter gradient was applied with a second HPLC to compensate the plasma fluctuations by lowering the organic solvent alteration entering the ICP.

The application of the developed counter gradient method was applied on a thermally aged electrolyte as well as on a battery electrolyte from a hybrid electric vehicle. Eleven peaks could be separated and identified with ion trap time-of-flight MS in thermally aged LIB electrolyte. The concentration of organo(fluoro)phosphates, which causes two of these peaks could be determined. In the electrolyte from the hybrid electric vehicle, only ionic and polar organo(fluoro)phosphates were identified.

Keywords: lithium ion battery, phosphoruos speciation

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THP-44 Validated procedures of isotope dilution ICP- MS coupled with HPLC for determination of selenium species in food samples

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Speciation analysis concerns the identification and determination of specific forms of an element in the studied material. The number of applications of high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) in speciation analysis is very advancing in this field. Although, in many cases qualitative information about form of element is inadequate, especially in trace analysis. Therefore, it is necessary to develop new analytical procedures that allow the separation and determination of forms of the element with the highest accuracy and precision and ensure to obtain validated results. Particularly challenging for speciation analysis can be modified direct isotope dilution mass spectrometry (IDMS) on-line coupled with HPLC. IDMS is regarded as a primary method of measurements and for total elemental analysis is well documented. Isotope dilution analysis in elemental speciation is a different matter and still a quite new issue. Two different approaches can be applied: the first is the species-specific ID mode and the second is species-unspecific ID mode. The main assumption of these modes is based on the measurement of isotope ratios in a sample, where its isotopic composition has been altered by the addition of a known amount of an isotopically enriched standard.

The aim of this study was to apply validated measurement procedures for the selenium species determination with the use of isotope dilution inductively coupled plasma mass spectrometry on-line coupled with HPLC. For the quantitative measurements of selenium species, the following samples were selected: onion, leek (different parts), garlic and vegetable sprouts. Validation approach in line with requirements of ISO/IEC 17025 and Eurachem guidelines was followed. Mathematical modelling of analytical processes and detailed investigation of all parameters influencing final results were adequate for validation of measurement procedures, establishment of traceability and estimation of expanded uncertainty.

Keywords: speciation, isotope dilution, HPLC, ICP-MS, selenium

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THP-45 Natural and ^{82}Se-labelled selenomethionine certified reference materials

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Two new candidate Certified Reference Materials (CRMs) for selenomethionine have been prepared by the National Research Council Canada. The material SENS-1 is a high purity natural isotopic abundance selenomethionine powder, whose purity was determined using quantitative nuclear magnetic resonance spectrometry with SI traceability. The second material, SEES-1, is an aqueous solution of ^{82}Se-labelled selenomethionine, which was synthesized in-house. Certification of the selenomethionine content of this material was conducted using reverse isotope dilution with high performance liquid chromatography – inductively-coupled plasma mass spectrometry, using SENS-1 as the primary standard. The process involved in the certification of these materials will be discussed and examples of the application of SEES-1 in the analysis of selenomethionine-containing samples of various matrices will be provided.

Keywords: certified reference material, isotope dilution, speciation, selenium

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THP-46 Speciation of arsenic in alcoholic beverages using LC-ICP-MS/MS

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The Canadian Food Inspection Agency contributes to the well-being of Canadians by ensuring the safety of domestic and imported food. Recently, concerns have been raised about wine produced in areas where soil and grapes may contain high levels of arsenic. This led to a national survey of both domestic and imported wines and other alcoholic beverages. Six arsenic species (AsC, AsB, MMA, DMA, As(III) and As(V)) were separated and detected in oxygen reaction mode by triple quadrupole LC-ICP-MS/MS using an additional mass filter to aid in the removal of interferences with arsenic. Calibration standards were matrix matched with 15% ethanol and a 1:1 dilution was applied to samples. A verification study for vermouth and spiced rum, using a previously validated method for red and white wine, indicated differences in recoveries for As(III) and As(V). Initially, this was thought to be due to matrix effects, however, additional testing revealed recoveries for some alcoholic beverages to be close to zero for As(III) and near 200% for As(V). Study results showed that As(III) converted to As(V) in varying degrees depending on the alcoholic beverage type. Efforts to prevent conversion of the species included: increased amounts of anti-oxidant in the sample diluent, increased sample dilution and decreased pH of the sample diluent. A slightly acidic sample diluent successfully prevented species conversion in all alcoholic beverages tested, with no negative impact on other arsenic species of interest. Data showing species conversion will be presented, as well as verification data for the method. A summary of the total and speciated arsenic data for the 300 alcoholic beverages collected in the Canadian national survey will also be presented. This method was capable of quantifying levels of six arsenic species in alcoholic beverages.

Keywords: arsenic, speciation, LC-ICP-MS/MS, alcoholic beverages

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THP-47 An Investigation on the influence of the chemical forms of arsenic for the accurate determination of total arsenic in rice

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Accurate determination of arsenic (As) has been an important issue for food safety because of its well-known toxicity. In fact, to assess the toxicity due to As, it is necessary to perform As speciation since the toxicity depends on its chemical form. However, when the total As in a sample is at the trace level below the maximum allowance of any arsenic species, the quantitation of total As is satisfactory for the toxicity assessment. In this work, the total As concentration in rice was analyzed by ion chromatograph inductively coupled plasma mass spectrometry (IC-ICP-MS). The sensitivity was found to vary significantly with the chemical form of As. Generally, the standard solution of arsenic has been made by As(V) standard. It might be good for the sample of which major species is As(V). But, if the major species of arsenic in a sample were different from As(V), the accuracy would not be reliable due to the different sensitivity. Thus, the standard should be selected carefully. This study showed the amount of total arsenic in a sample could be falsely obtained by the standard solution of different arsenic species. To our knowledge, the influence of the chemical forms on the analysis of total As has not been investigated so far. The different arsenic species used in this study were As(V), As(III), MMA, DMA and AsB. The accuracy of total As concentration in rice was also compared for the internal standards, Ge, In, Rh, Te, and Se isotopes. Among them, Te provided the best accuracy performance.

Keywords: arsenic species, total As, ICP-MS

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THP-48 Snapshots of metal speciation via liquid chromatography inductively coupled plasma mass spectrometry

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We have developed a bioanalytical method to analyze iron speciation by liquid chromatography (LC) coupled to inductively coupled plasma mass spectrometry (ICP-MS). Our LC-ICP-MS method allows for the direct quantification of administered intravenously iron nanoparticle drugs (sodium ferric gluconate, brand and generic) in clinical samples (blood plasma or serum), while simultaneously measuring the effect the released iron from the nanoparticle drugs has on the native iron species [iron proteins (i.e. transferrin, ferritin, albumin) and labile iron (iron citrate)]. Our methodology is fully validated per FDA guidance for bioanalytical method validation and offers a much-needed tool to track iron speciation pre- and post-infusion of intravenously iron nanoparticle drugs. We have further expanded our method to analyze the native metal speciation in plasma and other metal nanomaterials. This analytical method will be applied to analyze iron speciation in a clinical trial of healthy volunteers administered with the brand and generic sodium ferric gluconate.

Keywords: liquid chromatography, inductively coupled plasma, mass spectrometry, nanomedicines, non biological complex drugs, metal speciation

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THP-49 Feasibility study for the determination of arsenic species in nutritional products and raw ingredients by HPLC-ICP-MS

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In this collaborative study between Abbott Nutrition and Agilent Technologies, we report the results for arsenic speciation in raw ingredients and infant formula by using high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Hyphenated techniques utilizing HPLC-ICP-MS for elemental speciation is one of the fastest growing areas of research in atomic spectroscopy. Elemental speciation plays an important role in food safety. Arsenic is found in the natural environment (soil, water and air) and is a well known human carcinogen. The determination of the total form of arsenic only tells part of the story. For example, the toxicity of arsenic is strongly affected by its chemical form. The inorganic forms of As (arsenite (As(III)) and arsenate (As(V)) are generally more toxic than the organic forms of arsenic (dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA)). Other organic forms of arsenic such as arsenocholine (AsC) and arsenobetaine (AsB) are relatively non-toxic in humans. Therefore, their concentrations were not determined in this study. A total of 11 samples including four NIST standard reference materials (SRMs) were analyzed between two laboratories (Abbott Nutrition and Agilent-UC Davis Food Safety laboratories) using two different HPLC-ICP-MS instruments and different mobile phases reagents. Arsenic species (arsenite (AsIII), arsenate (AsV), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA)) in the samples were extracted with nitric acid by microwave-assisted extraction. Comparable results were obtained between both laboratories. The limits of quantitation for all species were approximately 2.5 $ng.g^{-1}$ and 5 $ng.g^{-1}$ in liquid and powder samples, respectively. Good linearity (R= 0.9995 or better) were also obtained for all species in calibration curves prepared by external standardization. The NIST SRMs results for all arsenic species, where certified limits were reported, were within the certified limits. Spike recoveries in all products and blank solutions ranged from 90-110 %. These preliminary results demonstrate that the Agilent 7900 ICP-MS when combined with the Agilent 1260 HPLC can determine low concentrations of arsenic species in infant formula and raw ingredients.

Keywords: arsenic, speciation, raw ingredients, nutritional products, infant formula, liquid chromatography, inductively coupled plasma, mass spectrometry

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THP-50 Simultaneous iodine and bromine speciation analysis in infant formula using HPLC-ICP-MS

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A simultaneous, fast and sensitive method for the analysis of iodine and bromine species in infant formula was developed using high performance liquid chromatographyinductively coupled plasma mass spectrometry (HPLC-ICP-MS). The method was used to determine the four halogen species (I^-, IO^-, Br^-, and BrO^-) in a NIST 1849a (Infant/Adult Nutritional Formula) standard reference material and four commercially available infant formula products from the United States and China. All 4 halogen species had baseline separated in less than 6.5 min using anion exchange resin column. Calibration for the four species was obtained from 0.1 up to 100 $\mu g.L^{-1}$ with linearity better than 0.9999 in all cases. The limits of detection for I^-, IO^-, Br^-, and BrO^- were all less than 0.6 $g.kg^{-1}$. To test the suitability of the method for the accurate determination of low concentrations of the four species in infant formula samples, a spike recovery test was carried out at 20 and 40 $g.kg^{-1}$. Total elemental determinations of iodine and bromine were also performed using only the triple quadrupole ICP-MS/MS.

Keywords: iodine species, bromine species, speciation, liquid chromatography, inductively coupled plasma mass spectrometry, infant formula

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THP-51 Application of ICP-MS technique for investigation of new possibilities in extraction of trace metals using NADES

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Natural deep eutectic solvents *(NADES)* are a new class of solvents obtained by mixing solid compounds that are not necessarily salts, such as choline chloride, sugars amino acids obtaining a eutectic mixture with a melting point much lower than the individual components. As the presented results reflect, NADES allow to prepare sample efficiently for speciation analysis of selected metals that play an important role in food and medical analysis. The proposed research gives new possibilities for speciation analysis and plays an important role in the biological and medical fields.

At the beginning the total amount of elements in young barley (*Hordeum vulgare* L.) was established as 16.69 0.22 $g.g^{-1}$ for copper, 156.29 0.82 $g.g^{-1}$ for manganese, 155.35 1.29 $g.g^{-1}$ for zinc, 9.10 0.21 $g.g^{-1}$ for molybdenum and 0.35 0.01 $g.g^{-1}$ for cobalt. The selection process of metals chosen for this study was based on their essential micronutrient element to most life forms. After that the most suitable solvents were identified, the determination of total and extractable amount of metals in young barley was carried out by inductively coupled plasma mass spectrometry (ICP- MS). In addition, a complementary analysis of extracted metal complexes was performed using chromatography coupled with inductively coupled plasma mass spectrometry method. It was confirmed that the NADES are able to extract different metal and metal species in comparison with commonly used solvents. The study indicated that extraction by using the NADES has been successfully applied for determination of metals and metal complexes in young barley.

NADES as functional liquid media can dissolve natural or synthetic chemicals of low water solubility. Additionally, NADES were applied to the solubilisation of wide range of biomolecules for example non-water soluble bioactive natural products (BIONPs), such as: gluten, starch and DNA. It has allowed to find answer to some of the fundamental biological questions for instance, how organisms deal with their non-water soluble BIONPs or lipid soluble metabolites?

Keywords: NADES, ICP-MS, extraction, zinc, copper

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THP-52 Development and validation of a method for ultra-trace speciation analysis of chromium in foodstuff by HPLC-ICP-MS using species specific isotope dilution

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Chromium speciation analysis at trace and ultra-trace levels in foodstuff has received great attention in the last years. Among the toxic trace metals of interest in food chemistry, chromium is one of the most problematic because it behaves as a valence chameleon. Whereas Cr(VI) has been recognized for several decades as being carcinogen, Cr(III) was long time considered as having beneficial health effects. Nevertheless, the European Food Safety Authority (EFSA) stated relatively recently (2014) that there is no convincing evidence of beneficial effects of Cr(III) for healthy people. Therefore, the interest in chromium speciation shifted relatively recently form focusing solely on Cr(VI) to the determination of both its species (Cr(III) and Cr(VI)).

Chromium speciation analysis in food is very challenging mainly because of the high instability of Cr(III) and Cr(VI) species. In addition, in food samples both chromium species are present at ultra-trace levels hence requiring the use of both sensitive and highly selective analytical tools. Online coupling of HPLC with ICP-MS by using species specific isotope dilution (SSID) has become, in the last years, the state-of-the art method for accurate chromium speciation analysis.

This work aims at the development of a truly accurate, rapid and efficient method for simultaneous speciation analysis of chromium (Cr(III) and Cr(VI)) in foodstuff by SSID in combination with HPLC-ICP-MS. A high efficiency sample introduction system (APEXTM) will also be employed for sensitivity enhancement in order to cope with ultra-trace levels of chromium species in food. Comparison of different analytical approaches for species quantification, such as external calibration, conventional and simultaneous isotope dilution approaches in various food matrices (milk, bread & cereals, meat) will also be addressed.

Keywords: chromium speciation, food, HPLC, ICPMS, species specific isotope dilution

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THP-53 Quantitative LA-ICP-TOF-MS bioimaging

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In this work, quantitative LA-ICP-MS was addressed in the field of (pre)clinical studies on metal based anticancer drugs. For this purpose, ICP-TOF-MS (TOFWERK AG, Thun, Switzerland) was combined with a low dispersion LA-setup enabling high-resolution multielemental images, down to single cell resolution, in a high throughput manner. More specifically, the novel tube-type Cobalt-cell (Teledyne Cetac, Omaha, USA) was implemented. The system featured single pulse response duration of > 200 Hz. The use of LA-ICP-TOF-MS enabled spot-resolved mapping with no spectral skew whereby the complete mass spectrum was recorded for every individual laser pulse, resulting into individual image pixels containing the full mass spectrum. We will discuss quantification in bioimaging based on this technique at lateral resolutions < 2m, discussing limits of detection and thus revealing those elements which can be addressed at single cell levels in typical (pre)clinical samples as such as tumor tissue and tumor spheroid models.

Keywords: laser ablation, time of flight mass spectrometer, cobalt cell, quantification, single cell resolution, high lateral resolution, high throughput

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THP-54 Complexation strategy for SEC-ICP-MS for the analysis of protein adducts with ethylmercury from thiomersal in influenza vaccines

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Human exposure to mercury species can be traced back to diverse sources. In case of ethylmercury ($EtHg^+$), exposure is strictly anthropogenic and derived from the use of ethylmercury thiosalicylate (Thiomersal, THI) as preservative in multi-dose vials of vaccines. THI decomposes in aqueous media and the following release of $EtHg^+$ leads to antimicrobial properties. Banned in the EU since 2001, multi-dose vials are still used in the USA and developing countries and contain approximately 25 g Hg as $EtHg^+$ per dose. The distribution pathways for $EtHg^+$ in the human body are not fully understood and still under discussion. Adduct formation of $EtHg^+$ with several blood proteins has already been indentified to contribute to the elucidation of $EtHg^+$-toxicokinetics. For these investigations, it is necessary to preserve molecular information of mercury-protein adducts during analysis, while separation of protein adducts and non-bound Hg has to be achieved. Size discriminating techniques, like size exclusion chromatography (SEC), coupled to elemental detection, like inductively coupled plasma-mass spectrometry (ICP-MS), are particularly well suited for this purpose. This study investigates the adduct formation of $EtHg^+$ from THI with the active ingredient in influenza vaccines, hemagglutinin (HA), which is a membrane protein of virions. Experiments have been carried out using a single-dose vaccine, incubated with different concentrations of THI and adduct formation was investigated by ultrafiltration and subsequent total reflection x-ray fluorescence (TXRF) analysis. SEC-ICP-MS was applied to obtain further information on the size of the protein involved in adduct formation. Since non-bound $EtHg^+$ adhered on the stationary phase of the SEC column and subsequent injections of thiol-containing compound showed false-positive results on the contaminated system, gradient elution using a thiolate as complexing agent was developed. Using this approach, it was possible to show adduct formation of $EtHg^+$ and HA. The use of a complexing agent allowed for quantification with THI and revealed that 0.56% of $EtHg^+$ binds to HA in multi-dose influenza vaccines under the selected conditions.

Keywords: SEC-ICP-MS, hyphenated techniques, mercury, vaccines

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THP-55 Elemental analysis of the changes in the metal profiles and arsenic species during wine processing

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Wine is one of the world's most popular beverages. Its quality depends on many different factors, including elemental content, which affects numerous stages of wine production. Various elements are needed to grow healthy vines and grapes while others influence the efficiency of alcoholic fermentation. On the other hand, some elements may not impact the organoleptic properties of wine, can still negatively affect human health, such as heavy metals and arsenic. The metal content of wine is comprised mainly of natural sources from the environment where the vines are grown. However, it is not entirely understood how anthropogenic contributions during wine production impact the final metal concentration in wine. Furthermore, it is unclear if arsenic species change during wine processing from their naturally existing profiles found in the berries. It is prudent to understand if conversions between the arsenic species occur during the production because inorganic and organic forms have different toxicities.

For this study, the effects of processing on arsenic species and metal concentrations were analyzed throughout the production of two wines at the UCD Teaching and Research Winery. The wines were produced from Cabernet Sauvignon and Merlot grape varieties. Samples were collected at strategic time points from harvest to bottling. Each sample was analyzed for four different arsenic species (arsenite, arsenate, monomethylarsonic acid, and dimethylarsinic acid) and 56 element profiles. The arsenic speciation was completed using an ion exchange high-pressure liquid chromatography coupled to a triple quadrupole inductively coupled plasma - mass spectrometer (HPLC-ICP-MS/MS). The method employed was a fast arsenic speciation method developed specifically for all wine types. The 56 element concentrations were obtained with a dilute-and-shoot method using the same ICP-MS/MS. This presentation will discuss the resulting element and speciation profiles and focus on the processing steps where the most significant differences were seen during wine production. By understanding how processing can affect the final elemental content of wine, winemakers will better be equipped to manufacture a more stable and higher quality product.

Keywords: arsenic speciation, winemaking, ICP-MS/MS, elemental analysis

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THP-56 Multi-elemental (As, Sn and Hg) speciation in wines by HPLC- or GC-ICP-MS

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The origin of trace elements in wine may be diverse : from natural to anthropogenic (herbicides/pesticides, atmospheric contamination,...) sources. If the total content of the trace elements in wine is quite well documented in the literature, depending on the element, the speciation data may be very scarce. Yet, it may directly depend on the source of the trace elements or be impacted by the use of bacteria and/or yeasts during the vinification process. The objective of our work was therefore to evaluate the speciation of different toxic elements in wine : As, Sn and Hg. The development and the validation of the different speciation methods (by HPLC-ICP-MS for As and GC-ICP-MS for Sn and Hg) will be presented. The results obtained from a set of more than 100 samples collected worldwide will then be detailed. An alternative use of the acquired speciation data for discrimination of the geographical origin will finally be introduced.

Keywords: arsenic speciation, tin and mercury speciation, wine

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THP-57 Lead in wine : total concentrations, speciation and isotopic signatures

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In wine, the presence of lead (Pb) is mainly related to atmospheric deposition of airborne particulate matter on grapes and/or also, to a lesser extent, by the intake of this element by the vine from the soil and the ground water. Wine could represent a source of Pb for the human diet. In response to these informations, the evolution of total Pb concentration requirements have been lowered over the last twenty years. In order to gain as much information as possible on Pb in wine, we have used a series of advanced analytical strategies to follow and identify the total lead content in wines. We have analyzed the total Pb content in a set of more than 100 wine samples by ICP-MS. Strong differences of Pb concentrations were obtained depending on the vintage, the oldest samples investigated (basically from the 70's and the 80's) presenting the highest lead content, suggesting an anthropogenic source of the Pb.

Further, in order to better understand the origin of this Pb contamination, the wines collected from the same area and covering 40 years of vintage (from 1969 to 2010) were more deeply investigated for speciation of the Pb species. The speciation analysis in these wines by GC-ICP-MS showed the occurrence of Me_3Pb at concentration levels lower than 1 $g.L^{-1}$ and decreasing from the beginning of the 80's. This pattern follows the phasing out of leaded gasoline in Western Europe.

Finally, to go deeper in the information to be gained from Pb isotoptic signatures, we have analyzed the isotopic signatures of the different lead species present in the wine to assess the origin of these Pb species. These developments were performed by hyphenated techniques using separation and detection by sector field mass spectrometers, either high resolution ICP- MS or high resolution MC-ICP-MS. The results will be presented and discuss for further and history of Pb levels in wines.

Keywords: lead in wine, speciation analysis, isotopic signature

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THP-58 Evaluation of a complete workflow for the determination of arsenic species in fish and rice

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In addition to the determination of the total arsenic content, the speciation analysis of arsenic compounds has become more and more common in quality control laboratories in the food industry. Beverages like apple or orange juice, wine and others can be diluted for simple and fast sample preparation. For groceries such as fish or rice, a more complex sample preparation is necessary. Besides dissolving the sample to completeness, it is crucial not to change or convert the species and by this lose this information.

Here we compare different sample preparation procedures with respect to digestion quality, recovery of the arsenic species and sample throughput. The samples were either mechanically destroyed using the SpeedMILL PLUS or digested using the TOPwave Microwave. By adding proteases (Proteinase K) lysis of the samples can be forced. HPLC-ICP-MS was used to analyse the arsenic species with ng.L^{-1} limits of detection. A precise comparison of the different workflows proves the applicability of the SpeedMill PLUS for easy, fast and accurate routine analyses.

Keywords: speciation, arsenic, HPLC-ICP-MS, fast, rice, fish, Analytik Jena, sample preparation

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THP-59 Development of SEC–ICP-MS/MS method to evaluate the formation of DNA-protein complexes

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The interactions DNA-protein are dynamic and reversible phenomena based on non- covalent bonds, which allow the propagation and the expression of genetic information. However, endogenous or exogenic factors such as free radicals, heavy metals... can induce the formation of covalent bonds between these 2 entities and lead to the formation of DNA-Protein Cross (DPCs) links. Because of their considerable size, DPCs are likely to block the processes of DNA replication, transcription and auto-repair and can lead to genetic mutations and cancers. However, the formation of DPCs is still poorly known, in particular because of the lack of analytical methods allowing their quantification.

An analytical method allowing detection and the quantification of DPCs was developed, by coupling a chromatographic separation and an ICP-MS/MS.

First results on the model system aptamer/thrombin are presented. The aptamer, thrombin and DPCs formed can be separated by size exclusion chromatography from small volumes of samples.

Detection and quantification was performed by ICP-MS/MS, using the sulphur resulting from the cysteine and methionine residues of proteins. The use of ICP-MS/MS was proved to be a good alternative to prevent interferences related to polyatomic ions.

The limits of detection and quantification of sulphur using such a hyphenated method were evaluated and found to be 0.02 $g.L^{-1}$ and 0.15 $g.L^{-1}$, respectively. For the system aptamer/thrombin, it corresponds to LOD (DPCs): 41 $pmol.L^{-1}$ and LOQ (DPCs): 0.36 $nmol.L^{-1}$ in terms of DPCs.

Since limits of detection of DPCs evaluated from other existing methods are in the $nmol.L^{-1}$ range, these limits are remarkable and prove that SEC-ICP-MS/MS appears as a valuable tool for DPCs quantification.

This method should also be applied to the element P, resulting from the DNA phosphate groups in order to achieve the unambiguous detection of DPCs.

Keywords: DPCs, SEC-ICP-MS/MS, sulphur

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THP-60 Comprehensive speciation analysis of metal complexes in coconut water as a model for method development for studies of plant endosperm metallome.

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Metals such as Fe, Mn, Ni, Zn and Cu play an important role in the life cycle of plants. These metals are essential for cellular functions, enzymatic activation, gene expression and metabolism of amino acids, lipids and carbohydrates, but in controlled amounts, because at higher levels they become toxic. Studies of the mechanisms developed by plants to control and regulate the absorption, transport and storage of metals require the development of analytical methodologies for the characterization of their chemical forms in liquids circulating in plants. However, the amount of plant liquids available for analysis is usually very low (several microliters range) which makes the initial testing of analytical procedures difficult. Thus, coconut (Cocos nucifera) water available in significant quantities was chosen as a model for method development studies of plant endosperm metallome.

The edible part of the coconut fruit (coconut meat and coconut water) is the endosperm tissue. The liquid part of the coconut endosperm called coconut water is a drink widely consumed in exotic countries. Coconut water, enclosed in its envelope, is sterile, rich in organic and inorganic compounds that contribute to its isotonic properties. Nutrients from coconut water are obtained from the seed apoplasm (surrounding cell wall) and are transported into the endosperm [1]. The chemical composition of coconut water was investigated in different varieties of coconuts at different stages of maturity of the fruit [2,3].

The analytical approach presented in this work is based on i) evaluation of metals total content, ii) separation of different species by hydrophilic interaction chromatography (HILIC) coupled with ICP MS and iii) in parallel coupling HILIC with electrospray-Orbitrap MS for the detection and structural identification of metal complexes. The quantification of metal species was carried out by in-situ ID ICP MS. The coconut samples of different origin, including Ivory Coast, Costa Rica and Thailand, were analyzed to evaluate the variability of speciation as a function of the culture environment.

The results obtained show the highest concentration of iron, nickel, copper, zinc and manganese in coconut water in samples from the Ivory Coast. The metal complexes detected include $Fe_3Cit_2Mal_2$, Fe_3Cit_3Mal, $Fe_3CitMal_3$ and $FeCit_3$, Cu-nicotianamine, $NiAsp_2$, Ni Mal_2 and Ni-nicotianamine, $ZnGln_2$, Zn-nicotianamine, $ZnHis_2$ and $ZnCit_2$.

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THP-61 Simultaneous analysis of selenium and arsenic in drinking water with LC-ICP-MS

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Good quality drinking water is vital for public health. To ensure it is safe for consumption, drinking water is routinely monitored for potentially toxic substances including heavy metals. Since the toxicity of some elements, e.g. arsenic and selenium, is strongly dependent on the chemical form or species in which it occurs, it is important to determinate the levels of the individual species. A method for the simultaneous separation and determination of selenate (SeVI), selenite (SeIV), selenomethionine (SeMet), selenocystine (SeCyS2), methylselenocysteine (MeSeCyS), selenoethionine (SeEt), selenourea (SeUr), arsenobetaine (AsB), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenite (As(III), and arsenate (As(V) in drinking water was established using high performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICP-MS). An Agilent ZORBAX SB-Aq reversed-phase column with a 20mmol.L^{-1} citric acid and 5mmol.L^{-1} sodium hexanesulfonate buffer solution (pH=4.4,adjusted with ammonia) with a flow rate of 1.0 mL.min^{-1} was used for separation and ICP-MS was used for detection. The twelve species were completely separated within 7.5 min. All the linear correlation coefficients of the twelve species were greater than 0.9995 and the detection limits were 0.15μg.L^{-1} 、 0.13μg.L^{-1} 、 0.15μg.L^{-1} 、 0.18μg.L^{-1} 、 0.12μg.L^{-1} 、 0.29μg.L^{-1} 、 0.25μg.L^{-1} 、 0.26μg.L^{-1}、 0.10μg.L^{-1}、 0.15μg.L^{-1}、 0.14μg.L^{-1} and 0.10μg.L^{-1} , respectively. The precision was blow 10% in all cases and the recovery rates ranged from 76.9%-106.2%. The method can be used for the quantitative determination of the twelve species in drinking water.

Keywords: selenium speciation, arsenic speciation, HPLC-ICP-MS

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THP-62 The formation of plant-based antimony nanoparticles by inorganic Sb species

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This study aims to determine the plant-based formation of Sb-nanoparticles *in vitro* and *in situ* by single particle ICP-MS analysis. In vitro experiments showed that leaves of terrestrial yellow box Eucalyptus sp. and semi aquatic Typha sp. produced Sb-nanoparticles, with great variation in particle size ranging from 30 to 100 nm and 30 to 90 nm, respectively. A linear relationship between Sb concentration and particle size was detected for both terrestrial and semi- aquatic plants. Terrestrial plants showed a good linear model when using the inorganic oxidised form Sb(V) (antimonate) to form Sb-nanoparticles. By contrast, semi-aquatic plants showed a good linear model when using the inorganic reduced form Sb(III) (antimonite). This suggests a preferential formation of plant-based Sb-nanoparticles based on plant type and Sb forms. *In vitro* plant-based formation of Sb-nanoparticles was not temperature dependent as there were no significance differences detected between different boiling methods. Preliminary *in situ* experiments showed that weed *Urtica dioica* (Stinging nettle) and native grass *Austrostipa* sp., growing on Sb- rich mineral waste, accumulated higher levels of Sb in various tissues parts. For instance, Stinging nettle accumulated nearly four times as much Sb in their root tissue compared to *Austrostipa* sp. with 3720 ug.kg^{-1} and 1000 ug.kg^{-1}, respectively. By contrast, above ground parts accumulated similar concentrations of Sb between plants species, 130 ug.kg^{-1} and 100ug.kg^{-1}, respectively. As for Sb nanoparticle formation, *Austrostipa* sp. produced bigger particle size in roots (118 nm) relative to shoots (83 nm); while Stinging nettle produce similar particle size between shoots and roots with 162 nm and 163 nm, respectively. Overall, the variation in particle size between *in vitro* and *in situ* methods suggests that mechanism of Sb-detoxification may play an important role in the variation of Sb-nanoparticles formation in plants. More detail testing of in situ Sb accumulation in *U. dioica* and *Austrostipa* sp. is required to determine the plant molecules and Sb forms involved in the Sb- nanoparticles formation for added value of phytoremediation approaches in heavy metal mineral- rich waste land.

Keywords: antimony, nanoparticles, ICP-MS, plants

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THP-63 Exploring the generation of volatile mercury species by cryotrapping with ICP-MS detection

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Mercury is one of the most closely watched pollutants in the environment. At the same time, it is a typical example of a pollutant for which a speciation information is of paramount importance. Therefore, sensitive analytical methods capable of mercury speciation analysis at natural levels are in great demand. Chemical volatile species generation (CVG) with preconcentration and separation of volatile species in a liquid nitrogen cooled cryotrap and ICP-MS detection has been explored. Compared to more traditional approaches such as gas chromatography after derivatization or liquid chromatography prior to ICP-MS, this technique can offer excellent sensitivity due to high introduction efficiency and preconcentration of analyte from relatively large volume of sample into few second short peak.

CVG conditions for individual species (Hg^{2+}, monomethylmercury and ethylmercury) were tested in order to find compromise conditions for all species with AAS detection. Efficiency of generation was characterized both by collection of Hg vapor in a gold amalgamator and subsequent determination by AMA-254 mercury analyzer and by careful comparison of sensitivity in ICP-MS after CVG and liquid nebulization. Also suitability of gas phase dryers for Hg species was tested.

Importantly, cryotrapping experiments revealed pronounced demethylation and deethylation of species in the course of CVG-cryotrapping-ICP-MS procedure at compromise conditions for efficient CVG of all species.

Keywords: mercury speciation, volatile species generation, cryotrapping, ICP-MS

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THP-64 Determination of selenoproteins in human serum from lung cancer patients by IDA-SEC-AP-ICP- QQQ-MS

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Lung cancer (LC) is one of the ten most common causes of death in the world inducing more than 1.3 million deaths per year [1]. Due to the fact that the majority of LC cases diagnosed are in advanced stages, the 5-year survival period is only 15%, [2] being necessary an early diagnosis to increase this rate [3]. Metabolic disturbances are associated to cancer appearance and development, increasing oxidative stress [4]. Oxidative stress is an imbalance between antioxidants and reactive oxygen species (ROS) including free radicals, which can cause irreversible damage at high concentrations through oxidative changes in lipids, proteins and DNA. To limit the damage caused by ROS, an antioxidant system formed by enzymatic and non-enzymatic system may interact with these species to regulate their production.

Selenium (Se) is an essential trace element which is part of important components of several metabolic pathways, including the antioxidant defense and immune systems [5]. Some selenium compounds are recognized as selenium species, they are transformed into selenide, a common intermediated metabolite, and then used for the synthesis of selenoproteins. Some studies have suggested a relationship between the altered expression of selenoproteins and cancer risk [6]. For this purpose, the study of selenoproteins in serum from LC patient could provide new contributions to the patology of LC.

In this work, a method for the simultaneous speciation of selenoproteins in serum using size exclusion chromatography (SEC) and affinity chromatography (AFC) with detection by ICP-QQQ- MS, using analysis by isotopic dilution (IDA) for analytes quantification (2D/SEC-AF-HPLC- SUID-ICP-ORS-MS) was development to determine the concentration of three important selenoproteins in serum from LC patients. Results showed lower concentration of eGPx in LC patients, while levels of SELENOP and SeAlb were higher in the cancer group. However, the results of the statistical test "one way ANOVA" showed that only eGPx and SeAlb were different significantly ($p < 0.05$) between the study groups (LC vs healthy control) and they could be potential biomarkers for the early detection of LC.

Keywords: lung cancer, selenium, speciation, selenoproteins

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THP-65 Metals traffic and metabolomic alterations caused by the antagonistic interaction of cadmium and selenium using organic and inorganic mass spectrometry

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Cadmium (Cd) is a widespread, highly toxic, environmental pollutant derived from natural and industrial sources, which is known to be accumulated in the human body, producing serious harmful effects in humans [1]. On the other hand, Selenium (Se) is an essential element for mammals, which is well known for its antagonistic interaction against cadmium toxicity, such as the prevention of oxidative stress induced by this element [2]. For this reason, the use of analytical methods to obtain massive information, such as metabolomic approaches combined with a study of metals homeostasis by means of inorganic mass spectrometry, are of great interest to evaluate the biological effects of the co-exposure of Cd and Se in mammals. A metabolomic workflow based on the use of direct infusion mass spectrometry (DIMS) and gas chromatography mass spectrometry (GC-MS) was applied in serum of mice to establish the alteration in the metabolic pathways and the defence mechanism triggered by Cd/Se exposure [3]. Moreover, metals homeostasis and trafficking between organs and serum of mice exposed to Cd and Se, have been evaluated by the determination of the concentration of metals by inductively coupled plasma mass spectrometry. This work, demonstrate for the first time that Cd exposure causes a decrease of all the elements studied in lung except itself. On the other hand, Se provokes trafficking from metabolically less active organs (brain, lung and testes) to others with greater metabolic activity (kidney), which also facilitates its excretion. On the other hand, important metabolic alterations have been detected in important metabolic pathways, such as energy and amino acid metabolism, degradation of phospholipidic membranes and free fatty acids. In conclusion, this work illustrates the high reliability of the integrated use of organic and inorganic mass spectrometry to deep insight into the fate of elements in exposed organisms, providing information about metal trafficking, interactions and homeostasis.

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Keywords: metals interactions, selenium, *Mus musculus*, toxicometabolomics

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THP-66 Investigation of arsenolipids in brain and muscle tissues of skipjack tuna using HPLC-mass spectrometry

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Arsenolipids are strongly linked to the marine environment, where they occur alongside water-soluble arsenic species, in appreciable quantities in various marine organisms, including fish. The origin of these lipophilic arsenic compounds, their biosynthetic pathway, and if they have a possible biological role are currently unknown. Arsenolipids are also under investigation in regard to human health, because some arsenolipids were shown to be highly toxic to human cells and to have the potential to cross the blood-brain barrier. In this study, we investigate the distribution and metabolism of arsenolipids in a top predator marine fish, which was naturally exposed to arsenic at environmental levels. Therefore, brain and muscle tissues from five specimens of Skipjack tuna (Katsuwonus pelamis), were individually freeze-dried and subjected to a sequential extraction procedure followed by analysis of arsenic species in water- and organic extracts using HPLC/ICPMS and HPLC/HR ESMS. Arsenolipids and their distribution, as well as water-soluble arsenic species, in the different tissues of five specimens of Skipjack tuna will be discussed.

Keywords: arsenolipids, HPLC, mass spectrometry, speciation analysis

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THP-67 Comparison of two sensitive methods for the quantification of Cr (VI) in surface and drinking waters with IC-ICPMS and LC-ICPQQQ

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Water-link is a drinking water company, located in the Antwerp region, which provides drinking water for over 2 million people in Belgium and the Netherlands. Surface water, coming from the River Meuse and transported to the catchment areas of our production sites by the Albert Channel, is purified to drinking water with a quality according to the EC regulation 98/83/EU. However, a relatively large number of companies are located alongside this channel and the possibility exists that these companies are pouring their waste water in the channel. Chromium is widely distributed in the environment due to its many industrial applications, e.g. in steel industry and galvanization. ICPMS studies show a varying concentration of total chromium in the raw water (0.30-12.60 µg/L), in drinking water the concentrations are below the quantification limit (0.07 µ g/l). Cr (III) is a nutrient for the human body at trace level, while Cr (VI) is highly toxic due to its high oxidation potential. The need to speciate this last compound at much lower detection limits (ng/l) is therefore necessary. Two methods were optimized, validated and accredited by the Belgian accreditation organization (Belac) according to ISO 17025, one using an ionchromatography instrument coupled to an ICP single quad MS and one using a bio-inert liquid chromatograph coupled to an ICP triple quad instrument. The validation results will be compared.

Keywords: speciation, chromium (VI)

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THP-68 Quantitative speciation analysis for the in vivo study of iron metabolism and bioavailability from formula milk fortified with isotopically stable enriched iron oxo-hydroxide nanoparticles

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Human breast milk is the ideal food for neonates. Under certain situations, breastfeeding might not be possible, so infant formulas specially designed to resemble the human milk are used as substitutes for infant feeding. Such artificial formulations are fortified with essential trace elements at higher concentrations than those levels found in human breast milk. However, the chemical species of essential elements, such as iron, are different from those naturally found in the human milk. Furthermore, it is well known that the chemical species of a given element define the extension of its absorption and bioavailability [1]. In this sense, new efforts are currently being made in order to find an efficient iron fortifier for formula milk. A promising alternative arises from the use of mineral nanoparticles.

In this study, the bioavailability and metabolism of isotopically labeled 57Fe(III) oxo- hydroxide nanoparticles from formula milk were evaluated in lactating rats. Quantitative iron speciation in rat erythrocytes, serum and liver were performed by high performance liquid chromatography (HPLC) coupled to post-column isotopic dilution analysis (IDA) and inductively coupled plasma mass spectrometry (ICP-MS). The quantification of endogenous (natural Fe) and exogenous iron (57Fe) were calculated by applying the Isotope Pattern Deconvolution (IPD) methodology. The speciation analysis demonstrated that 57Fe was distributed into the body iron compartments (functional, transport and storage) associated to the main proteins implicated in iron metabolism (hemoglobin, transferrin and ferritin-like species). The observed degrees of incorporation of exogenous Fe from nanoparticles were around 50% in erythrocytes and liver and 60% in serum, being higher than those degrees observed for ferrous sulphate [2], the most common iron fortifier. The results indicate the potential of this nanoparticle to be used as a bioavailable source of iron.

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Keywords: iron, quantitative speciation, nanoparticles, bioavailability, HPLC, ICP, MS, Isotope Pattern Deconvolution (IPD)

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THP-69 LA-ICP-MS in Brain Imaging

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Two applications of LA-ICP-MS in brain imaging are presented. First, we studied blood- brain barrier (BBB) disruption in a mouse model of impact concussion. No biomarkers or treatments are currently available to diagnose, monitor, prevent, or delay posttraumatic neurodegeneration and allied brain pathologies. In this study, we investigated if dynamic contrast- enhanced MRI (DCE-MRI) with gadofosveset trisodium (a gadolinium-based contrast agent that binds serum albumin) can detect and track changes in the structure and function of blood vessels in mice after closed-head impact injury and used LA-ICP-MS to map spatial distribution of Gd in 10 μ m thick coronal sections of mouse brains harvested 2 weeks post-injury to confirm that the detected DCE-MRI abnormalities represented true BBB permeability dysfunction. Laser ablation system (LSX-213, Teledyne CETAC Technologies, Omaha, NE) was coupled to a quadrupole inductively- coupled plasma mass spectrometer (iCAP-Q, Thermo Fisher Scientific, Waltham, Massachusetts). The samples were scanned line by line with the following scan parameters: the spot size – 20 μm, distance between lines – 0 μm, scan speed – 40 μm/s. Images were processed using an in-house MATLAB program (Mathworks, Natick, Massachusetts). Gd maps of brains obtained from impact-injured mice revealed enhanced Gd accumulation that colocalized with T1-weighted hyperintensities and BBB disruption detected by DCE-MRI. Our results provide "proof of concept" feasibility validation of DCE-MRI for diagnostic evaluation of BBB dysfunction in the acute- subacute period after closed-head impact injury.

In the second study we investigated gadolinium deposition in cerebral cortex in humans and rats after repeated exposure to intravenous gadolinium-containing contrast agents. Despite an explosion of published studies and intense clinical interest in this topic [1-4], little is known with regards to the mechanism of Gd deposition, given its accumulation in the brain, even in the absence of blood brain barrier compromise. Cerebral cortex plays critical role in cognitive processing (learning, memory), neuropsychiatric disorders, behavior regulation and it is known to be very sensitive to toxicants. For this study we used the following scan parameters: the spot size – 50 μm, distance between lines – 0 μm, scan speed – 100 μm/s. Analytical calibrations were performed with a reference standard (SRM 612, NIST, Gaithersburg, MD, USA) and 10% gelatin standards doped with Gd as a matrix-matched material. In order to elucidate the anatomy corresponding to Gd mapping, haemotoxylin and eosin (H&E) staining was performed on adjacent slides. The purpose of this study was to precisely map cortical deposition patterns in the rat and human brain, given the functional importance of this portion of the brain. Furthermore, the potential relationship between iron metabolism and Gd deposition is analyzed.

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Keywords: LA–ICP–MS, brain imaging, bioimaging, gadolinium–based contrast agents

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THP-70 Rapid determination of lithium ion battery materials using ICP-OES

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Lithium carbonate and nickel cobalt manganese oxide are important materials used in the manufacturing of lithium ion batteries. Since the quality of materials affects the performance of the battery, any elemental impurities need to be controlled at a low level. ICP-OES is a widely used atomic spectrometry technique for the measurement of trace elements. When using ICP-OES to measure these high lithium materials, the results for Na and K are biased high due to the interference of easily ionized elements (EIEs) and other impurity elements tend to be lower. However, EIE interferences can be reduced or eliminated using a vertical torch, combined with the cooled cone interface (CCI) technique. Using matrix matching and axial mode, the spike recoveries of all measured elements were in the range of 90-110%. For the nickel cobalt manganese oxide, the ratio of the major elements is very important, because it determines the energy density of the lithium ion battery. Using radial mode and the vertical torch to provide a high matrix capability, the maximum concentration of the standard curve can reach 900 ppm. Extending the concentration range minimizes the dilution factor and avoids errors caused by dilution. The analytical results were consistent with theoretical values for nickel cobalt manganese oxide. Also, the relative standard deviation of the long-term stability over 2.5 hours was less than 1%.

Keywords: lithium carbonate, ternary cathode materials, cooled cone interface

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THP-71 Analysis of complex metal oxide thin films by online-LASIL with ICP-MS detection

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is an established method for the analysis of solid samples. The possibility to obtain laterally resolved and depth information is of great interest for many research fields. Due to matrix effects in the ablation step as well as the ionization step, matrix matched standards are obligatory for quantification. For novel materials used in renewable energy sources (*e.g.* solid oxide fuel cells, solid state Li ion batteries), such matrix matched standards are not commercially available. Therefore, in-house produced standards are necessary.

Recently we presented a new method to overcome this drawback of the classical LA-ICP- MS technique. This approach is called online laser ablation of solids in liquids (online-LASIL) where the He carrier gas is replaced by a liquid (*e.g.* H_2O) to transport the particles produced in the ablation step into the detection system. The big advantage of this technique is the possibility to use aqueous standard solutions for signal quantification, because the yielded nanoparticle suspensions can practically be treated like liquid solutions. With this procedure, the advantages of the conventional liquid measurement and solid sampling approaches can be combined. Application of this technique for the stoichiometry analysis of STO thin films has been published recently **[1].**

As a result of continuously improving the LASIL system, we are now able to use the advantages of ICP-MS as detection device (*e.g.* higher sensitivity, faster data acquisition). By using an improved cell design and more suitable flow injection components, easier sample handling and a faster washout could be achieved. These improvements allow laterally resolved analysis of larger sample areas. Complex metal oxide thin films (CMOs) will be used to demonstrate the imaging capabilities of the online-LASIL technique.

Keywords: online, LASIL, laser ablation of solids in liquids, complex metal oxides, CMO, ICP-MS

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THP-72 Determination of Ba, Cs, Mo, Zr and U in SIMFuel samples by ICP-OES and ICP-MS for the study of fission products behavior during a nuclear severe accident.

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The development of realistic models for fission products behavior during a nuclear severe accident requires experimental data on fission products speciation into the fuel. In this context, several batches of dense UO_2 samples containing fission products surrogates under different chemical forms have been prepared and sintered, to be further submitted to thermal treatments in order to characterize fission products speciation under controlled temperature and oxygen potential conditions.

To that end, a large number of as-fabricated samples from these experiments were analysed by ICP-OES and ICP-MS after dissolution. A separation step by liquid chromatography on UTEVA resin was essential before the ICP-OES measurements to overcome the problems of spectral interferences and matrix effects caused by uranium.

This study emphasizes the complementarity of these two techniques in nuclear fuel characterization. The advantage of the ICP-OES analysis on simultaneous device will be explained in details. The importance of the integrated collision reaction cell in ICP-MS to avoid many problems of polyatomic interferences for the quantification of Cs and Ba will be highlighted.

The results of chemical quantitative analysis obtained by ICP-OES and ICP-MS are very important and they allowed acquiring valuable information for the continuation of the study. Indeed, the dispersion of the additives in the UO_2 matrix after sintering is not homogeneous in the pellets. The initial mixing of the different powders has not been effective. This is demonstrated by the chemical characterizations performed on several pellets from the same initial batch which showed that the final amount of additives varied a lot from a sample to another. Moreover, important Cs and Mo release took place during the sintering.

Keywords: SIMFuel samples, fission products, ICP-AES, ICP-MS, nuclear field

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THP-73 Metallurgical analysis with Avio 500 ICP-OES: dealing with matrices and interferences

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For the determination of trace elements in metallurgical matrices, ICP-OES is a commonly- used technique due to its ability to handle high levels of dissolved solids without the need for special sample introduction components or matrix separation schemes. Despite this advantage, the analysis of trace metals in metallurgical matrices also presents a challenge for ICP-OES: spectral interferences. Several elements present at high levels in metallurgical matrices have many emission lines (*i.e.* approximately 20,000 for iron), which increases the potential for spectral interferences. This work demonstrates the ability of the Avio 500 ICP-OES to overcome matrix and interferences effects to measure impurities in metallurgical matrices. The PlasmaShear, used to effectively cut off the tail of the plasma, allows the axial window to remain clean. The use of PerkinElmer's exclusive Multicomponent Spectral Fitting algorithm removes spectral overlaps induced by the matrices. Combining these features allows accurate and stable analysis of impurities in metallurgical matrices, including both pure and mixed metals.

Keywords: metal analysis, ICP-OES, data treatment, matrix effect, interferences

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THP-74 The evaluation of aluminium magnesium hydrotacite concentrations in Ziegler-Natta polymerized polyolefins for the prediction of discolouring processes

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Today, the worldwide production volume of plastics, elastomers and rubbers produced from olefins with Ziegler-Natta catalysts covers an extremely wide variety of applications. Technically, before a polyolefin material from the reactor is suitable for its intended application, it still needs to undergo several processing steps. The elevated temperatures, shear and exposure to oxygen can cause degradation processes that have a major impact on the polymer melt as well as the mechanical and aesthetic properties of the final article. By selecting the right stabilizing additives, these negative effects can be largely prevented. The basis of a typical additive package for polyolefins includes primary (phenolic-), hindered amine stabilizers and secondary antioxidants (phosphites or phosphonites) but as well acid scavengers. A common acid scavenger used in polyolefins is synthetic hydrotalcite, $Mg_6Al_2CO_3(OH)_{16}{\cdot}4(H_2O)$, which are layered double hydroxides well known for their anion exchange properties and deactivation of catalyst residues in polyolefins. Hydrotalcite is a layered double hydroxide (LDH) comprising an unusual class of layered materials with positively charged hydroxide layers and charge balancing, mobile anions located in the interlayer region. This structure gives these material anion exchange properties. The key functionality of hydrotalcites is the irreversible adsorption of residual acidic substances that originate from catalytic polymerization processes used to produce polyolefins and act as corrosion inhibition in polymer- based coating systems and adhesives, which increases protection of metallic surfaces against corrosive anions.

By doing so, hydrotalcites prevent many damaging side effects, most notably corrosion of processing equipment and degradation of the polymer itself. However, their concentration in polyolefin needs to be checked regular due to potential adverse effects. In this case study, we evaluated the yellowing defect on 2 PP pellet sample batches from closed bags stored after production for a few weeks and absence of direct UV light. We evaluated 2 populations, defect PP pellets appearing yellow and reference clearly white PP pellets

After acid digestion, ICP-OES measurements (INTEGRA XL ICP-OES GBC, Australia) have been performed in double. The defect yellow PP population had an elemental content of 79,6 8,0 $mg.kg^{-1}$ for Al, 100,0 10,0 $mg.kg^{-1}$ for Mg, covering a MgO/Al_2O_3 ratio of 3,18. While the reference non-yellow PP population had an elemental content of 54,1 6,0 $mg.kg^{-1}$ for Al, 66,6 7,0 $mg.kg^{-1}$ for Mg, covering a MgO/Al_2O_3 ratio of 3,11. Both populations had a similar MgO/Al_2O_3 ratio indicating for both the same hydrotalcite presence however the defect yellow PP samples did contain a 1,5 fold higher hydrotacite content. The elevated concentration of alkaline hydrotacites in the yellow defect PP pellets might have an impact on the alkalinity of the material.

Beside the elevated alkalicity in the samples, the additive stability has been influenced resulting in the yellow appearance of the defect samples. By using direct inlet-mass spectrometry on sample extracts from both populations, the presence of di-tertiary butylphenol (BHT) and di-tertiary butylquinone methide (BHT-QM) could be confirmed. Organic identification was done from toluene extracts by using the direct inlet device (Shimadzu, Japan) coupled with a 2010QP plus mass spectrometer (Shimadzu, Japan) in electron impact ionization mode (70 eV). BHT is a potential yellowing substance while the BHT-QM form of BHT appears yellow. The degradation of the antioxidantIrganox3114(1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine- 2,4,6(1H,3H,5H)-trione) under alkaline conditions was confirmed to evolve BHT and BHT-QM.

Keywords: yellowing, hydrotalcites, direct inlet, mass spectrometry

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THP-75 Validation of limits of quantitation in seawaters and brines by HR-ICP-OES

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The direct elemental analysis of saline matrices using ICP techniques in routine laboratories is challenging in respect to: (i) achieving good signal stability with low signal to noise levels, (ii) ionization interferences of alkali and alkaline earth metals that often lead to intensity deviations in the range from 5 to 10%, and (iii) maintenance issues, memory effects, and short lifetime of glassware and clogging.

Since saline matrices are used for various purposes, a large number of elements with limits of detection as low as possible are of interest. Due to its high sensitivity, ICP-MS is typically the method of choice to achieve limits of detection in the ppt range. However, ICP-MS typically tolerates matrix concentrations not higher than 0.3%, which requires high dilution of the samples. Thus, matrix specific limits of detection are compromised depending on the applied dilution factor. In general, ICP-OES instrumentation is more matrix tolerant compared to ICP-MS. The comparatively low sensitivity of conventional ICP-OES, however, hampers achieving sufficiently low limits of detection.

This work demonstrates the capabaility of an HR-ICP-OES to quantify sub-ppb levels of a wide range of elements in saline matrices such as seawaters and brines.

Keywords: ICP-OES, seawater, brine, limit of quantitation

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THP-76 Determination of trace elements in line-rich matrices using HR-Array ICP-OES

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Due to their unique properties, rare-earth elements (REEs) became of great importance in many areas of human endeavor. Since REEs possess very complex emission spectra they are difficult to quantify in the presence of one another using inductively coupled plasma optical emission spectrometry (ICP-OES). Here we present the application advantages for trace element analysis in REE materials originating from the superior optical resolution and high sensitivity of the PlasmaQuant® PQ 9000 Elite system. Additionally, the benefits of the implementation of powerful software tools (ABC, CSI) for background correction and correction of spectral interferences are demonstrated.

Keywords: ICP-OES, high resolution, REE materials

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THP-77 Laser ablation chemical mapping of high efficiency Kesterite solar cells with lithium alloying

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Enhancement of solar cell efficiency, by means of alkali-doping, is well-known for chalcogenide thin-film such as $Cu(In,Ga)Se_2$ (CIGS) or $Cu_2ZnSn(S,Se)_4$ (CZTS–kesterite) absorbers. Contrary to heavier alkali elements, lithium is expected alloying with the kesterite phase. Li-doping, leading to $(Li_xCu_{1-x})_2ZnSn(S,Se)_4$, offers a way of tuning the solar cell's efficiency by changing the Li/(Li+Cu) ratio. The detection of the Li/(Li+Cu) ratio, ranging from x = 0 to 0.12 in the first two microns below the surface is a critical analytical task. Therefore, a depth-resolved microanalytical method of Li-doped CZTS was developed, using laser ablation inductively coupled plasma mass spectrometry. Due to the polycrystalline morphology of the sample, with a porous structure, the elemental depth profiling was complex. For instance, an increase in grain size is observed for Li/(Li+Cu) ratios up to 7%. Finally, the laterally resolved detection of the Li ("mapping") could help to monitor the Li-doping homogeneity. The results were compared with other microanalytical laser techniques, such as LIBS, or laser ablation with an X-ray laser.

Keywords: solar cell, depth resolved micro analytic, chemical mapping, LA-ICP-MS, X-ray laser

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THP-78 High precision with ICP-OES - What is possible in real examples and in routine ?

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Up to now, ICP-OES has mainly been used for the determination of trace and minor components. For the determination of the main components, a very high demand is placed on precision and accuracy, which until now could only be met by classical wet-chemical methods.

Thanks to advances in semiconductor technology, today's ICP-OES systems enable new methods of instrument control and measurement data acquisition and evaluation.

In this lecture, practical examples will be used to show how ICP-OES can be used for the analysis of main components with the highest precision and therefore can replace the very complex wet chemical processes.

Keywords: ICP-OES, precision, accuracy, uncertainty

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THP-79 Ultra trace analysis in high purity materials by ICP-OES

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ICP-OES has been used for many years for the analysis of traces in the ppm range in base metals. However, if ultra traces in the ppb range have to be analyzed, very complex and expensive analytical instruments such as GD-MS, ICP-MS or GF-AAS have been used so far.

It is mainly due to advances in semiconductor technology that today's ICP-OES systems achieve higher performance.

This poster will show practical examples of how ICP-OES can be used for the analysis of ultra traces in the ppb range.

Keywords: ICP-OES, base metal, traces

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THP-80 Multiscale elemental analysis of buried materials and interfaces

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Elemental analysis of buried interfaces in multilayered structures (for instances conversion layers under organic coatings or hybrid organic/inorganic solar cells) and encapsulated materials is extremely challenging. Two analytical techniques offering quick insight into materials – micro XRF and glow discharge optical emission spectrometry - can help to optimize and control the manufacturing processes and understand failure causes.

Micro XRF, offering both transmission and fluorescence images directly, permits to measure encapsulated electronic components without preparation as the probing beam consists of X-Rays that could penetrate deeply in polymers and not electrons. At the same time the lateral resolution of micro XRF can be as good as 10 µm but depth resolution is limited.

On the other hand, glow discharge optical emission spectrometry relies on a plasma to sputter the material of interest and excite the sputtered species offering fast elemental depth profiles. The technique measures all elements (including H, Li, C, O, N) with nanometre depth resolution but it has no lateral resolution. Ultra fast sputtering of organic layers is achieved by adapting the plasma gas nicely revealing embedded layers. Synergies and complementarities of the techniques will be described and examples of applications presented.

Keywords: micro XRF, glow discharge optical emission spectrometry, buried materials and interfaces

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THP-81 Direct solid sampling process accompanying analysis with ETV-ICP OES - Monitoring the feedstock quality of coal conversion processes

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In the energetic and material use of energy feedstocks like coal, the knowledge of the inorganic compounds is fundamental for the optimization of the process efficiency. Inorganic compounds in solid fuels like coal and biomass have a possible negative influence on system performance and emission. Depending on their absolute concentration and in relation to each other, inorganic compounds in coals are sources of forming heat transfer degrading deposits and high temperature corrosion of materials. Therefore, the understanding of the chemistry associated with the evaluation of the coal quality is necessary for the processing industry to predict the process behavior of coals.

In addition to the problems during processing, the total element contents as well as the knowledge of their distribution is required to determine the suitability of a particular coal treatment or cleaning strategy. As a result of this, there is a growing need for rapid analysis methods to assess the total content as well as the element distribution in energy resources.

There are various methods necessary for the comprehensive characterization of coals. These traditional methods are often very time-consuming and they require an extensive sample preparation
– which makes them unsuited for a fast process-accompanying analysis.

Within bilateral industrial projects and a BMWi-founded joint project, the focus of development is on a process-accompanying technique with ETV-ICP OES to monitor the quality of energy fuels in the combustion process in power plants. This direct solid sampling method provides fast multi-element analysis from trace elements like Hg in the ppb-range to main components like O and S simultaneously. Furthermore, the temperature-dependent release of elements enables the rapid identification of elements in potential deposit-forming temperature ranges and the determination of species for some elements (pyrite/organic sulfur; oxygen from silicates or clay). The inclusion of this technique in a prediction model should give recommendations for the reduction of slagging and deposits in lignite-fired power plants and as a result a higher efficiency of the combustion process.

Keywords: ETV ICP OES, coal process analysis

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THP-82 Variable volatility of organic analyte forms in direct analysis, using ICP-OES, HR-CS FAAS and HR- CS MAS - drawback or benefit?

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The dependence of analytical signal of an element on its chemical form is evaluated as a serious limitation, when total content of the element is determined using atomic spectrometry techniques **[1-6]**. Such a situation can occur in direct analysis of organic solutions of samples (like petroleum products, fuels, biofuels and edible oils) dissolved in an organic solvent and directly aspirated to a plasma or to a flame. Variable volatility of various organic analyte forms causes variability of enrichment of gaseous phase in the analyte, as for more volatile analyte form, the content of analyte in gaseous phase is higher and the analytical signal is higher, than for less volatile compounds. In the most advanced studies in the field, silicon was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) **[1-2]**. It was found that total consumption system with heated spray chamber was necessary to overcome analyte speciation effect **[2]**. However, the analytical problem is usually neglected in both scientific research and routine analytical work.

The aim of this study was comparative research of analyte volatility effect using conventional ICP-OES as well as high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) and high-resolution continuum source flame molecular absorption spectrometry (HR-CS FMAS). In the case of the last two techniques the same equipment was applied, which gives opportunity to judge on the mechanism of the occurring processes. Silicon, the only element, which can be determined using both HR-CS FAAS **[3]** and HR-CS FMAS **[4]**, was the main analyte in this work. In some experiments, sulphur was determined (HR-CS FMAS **[5]**), as well as nickel (HR-CS FAAS). Various forms of analytes were investigated, including hexamethyldisiloxane (b.p. 101 ˚C), carbon disulfide (b.p. 46 ˚C) and nickel(II) 2,3,7,8,12,13,17,18-octaehtyl-21 H, 23 H-porphine.

Wavelength dispersive X-ray fluorescence was applied as an alternative technique, which signal does not depend on the analyte compound. In the case of volatile analyte forms, overestimated results of analysis using ICP-OES, HR-CS FAAS and HR-CS FMAS are expected, which can be utilized to acquire information on the presence of the volatile analyte forms in the investigated sample **[6]**.

Keywords: analyte form, speciation, organic solution, silicon, ICP-OES, HR-CS FAAS, HR-CS FMAS

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THP-83 Towards a greener approach for microwave assisted acid digestion of refractory petroleum crude samples using a single reaction chamber system followed by ICP techniques

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Elemental analysis in the petroleum industry has become of major importance due to the impact of metals and non-metals have on the whole value chain of the business. By knowing the trace metals present in petroleum feeds could be useful information to establish the relationship between its formation in reservoirs and its refinement into different products **[1]**. Additionally, the relevance of the data provided by this type of analysis has become a routine practice in the oil industry. Therefore, most of the methods reported so far are accomplished by spectroscopic methods after sample dissolution **[2]**. For petroleum feeds and products, different approaches for sample preparation are commonly using as standard methods **[2-5]**. Conventional wet acid digestion methods (hot block or MW assisted) are no doubt the most common choice today for performing trace element analysis of hydrocarbons on ICP based techniques. However, over the last two decades, in many high-volume laboratories facilities, direct injection of organic solutions has become widely used for the analysis of different feed such as whole crude, middle distillates, lubricant oils, among others **[6]**. Nevertheless, for complex feeds such as heavy oil, petroleum residues, deposits, asphaltenes, cokes high digestion efficiency is required **[7]**. To accomplish this requirement, a combination of concentrated reagents with high temperature and pressure has been an effective way to decompose these type of refractory samples **[8]**. With the advances on MW systems used for acid digestions (sequential systems, multimode and single reaction chamber technology) in combination with a better understanding of the chemistry **[9-10]** associated with the digestion process, the use of diluted acids in combination with oxidizing reagents have been reported as a green approach to digest different materials **[11-13]**. This approach has also been extended for petroleum products and derivatives [13] and biodiesel **[14]**. The present work will illustrate how this greener approach can be applied to a refractory petroleum sample that requires concentrated acids mixtures in combination with high temperature and pressure to ensure complete digestion. Effect of acid concentration, H_2O_2 as an oxygen source, MW temperature, pressure and residence time were evaluated during the sample preparation. Residual carbon content (RCC) and residual acidity after MW digestion were determined for the digestates. Finally, more than twenty elements were analyzed by ICP-OES whose recoveries using SRMs will be presented.

Keywords: microwave, single reaction chamber, acid digestion, petroleum, ICP

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THP-84 Determination of chlorides in crude oils by direct dilution using ICP-MS/MS

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The presence of chlorides in petroleum crudes needs to be monitored because it is necessary to control the presence of these salts before entering into crude oil refining units. During crude oil extraction and production, water associated with this processes contains chloride salts such as $MgCl_2$, $CaCl_2$, and NaCl which are drawn from crude oil wells along with hydrocarbons. The concentration of these salts in the crude oil varies from oil field which the crude is extracted and it can be present within the range of 3 to 300 pounds per barrel **[1]**.

Previous studies have shown that inorganic chlorides may be hydrolyzed to form HCl gas during industrial distillation of desalted crude oil. Water can dissolve the HCl gas to form dilute hydrochloric acid that can cause fouling and corrosion of equipment **[2-4]**. During preheating, if crude oil reaches temperatures of more than 248 ˚F (120 ˚C), these chloride salts break down to HCl, which is extremely corrosive **[1]**.

Additionally, organic chlorides could also be present in crude and they are impossible to remove using conventional salt separation process in desalting vessels; they decompose into HCl in the preheating process and cause severe corrosion in either overhead or downstream units **[1,5]**. To avoid corrosion, the concentration of organic chlorides in crude oil should be less than 1 $mg.L^{-1}$, despite that, their concentration in most of the crude oils tends to range from 3 to 3,000 $mg.L^{-1}$ **[1]**.

Therefore, having a reliable chloride concentration measurement in crude is critical because it serves as a primary indicator of potential impact in refining facilities associated with corrosion. Refineries spent millions of dollars annually in corrosion mitigation to guarantee safer operations and cost discipline.

Portfolio of analytical techniques to quantify chloride in crude, as well as different standard methods, are available. Spectrometric methods play an essential role because their simplicity and ability to be applied in conventional laboratories facilities as well as remote field areas **[6]**.

Inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), X-ray fluorescence spectrometry, have been used for the total quantitation of chloride in a variety of crude petroleum samples **[6]**. Additionally, combustion ion chromatography (CIC), coulometric titration methods have also been widely used.

Particularly, for single quadrupole ICP-MS technology, chloride determination could be impacted by the presence of sulfur and polyatomic interference; it is found that high bias is more dominant a sulfur concentration above one wt %. The introduction of the triple quadrupole technology (ICP-MS/MS) or commonly named tandem ICP-MS/MS, equipped with two quadrupoles and a collision/reaction cell, has demonstrated to handle useful spectral overlap as well as several cases of isobaric overlap, reducing unwanted reaction and improving analysis of many isotopes effective **[6]**.

The present work will present the results obtained on the determination of chloride in crude by direct dilution using tandem ICP-MS/MS. The figure of merit will be presented using the standard reference material such as NIST 1634c (Trace Elements in Fuel Oil) as well as results using a suite of crude oil samples having different characteristics. Comparison between single quadrupole *vs* tandem will be addressed a final comparison with other techniques.

Keywords: ICP-MS/MS, crude oil, chlorides

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THP-85 In-service oil analysis with ICP-OES following ASTM D5185

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Globally, heavy machinery is used in a wide variety of areas and industries. A key to keeping the equipment up and running is monitoring the lubricants for their metal content to track the trends of key wear metals, which can indicate when maintenance is required. ASTM has written method D5185 for the analysis of 23 metals in in-service oils by ICP-OES. This work will discuss the analysis of in-service oils following the guidelines in ASTM D5185.

Keywords: in, service oils, ICP-OES, ASTM D5185

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THP-86 Ethanol direct analysis of phosphorus, sulfur, copper and iron with the Avio 500 ICP-OES

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Ethanol is an important blending component in fuels which is commonly used in gasoline/petrol. Depending on the ultimate use of the fuel, the ethanol concentration can vary from
< 10% up to 85%. Because of its wide use, it is important to monitor the concentrations of impurities in the ethanol which can negatively impact the performance of the resulting fuel. As a result, standards have been established to evaluate those impurities in fuel by measuring the phosphorus (P), sulfur (S) and copper (Cu) content. Ethanol analysis by ICP-OES can be challenging both due to volatility and high carbon content. The low boiling point of ethanol (78 °C) means that a large volume of ethanol in the gaseous form enters the plasma, which may produce plasma instability and can ultimately extinguish the plasma. The high carbon content can deposit on the instrument interface or injector, which can lead to signal degradation over time. This work demonstrates the ability of the Avio 500 to measure low levels of P, S, Cu, and Fe in ethanol in accordance with ASTM D4806 and IP 581. By selecting the appropriate sample introduction and plasma conditions, low concentrations of P, S, Cu, and Fe can be accurately measured directly in ethanol, without the need for dilution or additional oxygen gas. Multicomponent Spectral Fitting (MSF) algorithm is used to eliminate the spectral interference on S at 180.669 nm, allowing accurate results to be obtained at concentrations as low as 100 $g.L^{-1}$.

Keywords: ethanol direct analysis, impurities, Avio 500 ICP-OES

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PLF-1 Method development for single cell analysis by use of ICP-MS

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An overview about different analytical techniques will be presented of how to investigate metals in individual biological cells by use of ICP-MS for detection, imaging or quantification of metals at cellular levels.

By use of laser ablation, we have investigated the up-take of nanoparticles by single cells in an imaging mode of operation. For matrix matched calibration, liquid suspension standards are blotted onto nitrocellulose membranes **[1]**. The quantitative results are validated by microwave digested cell samples. Additionally, we have developed staining techniques to visualize protein and DNA distributions in single cells and for identification of the cell status immunoassays based on metal-tagged antibodies **[2,3]**. New research based on cell arrays and detection of metal-tags by LA- ICP-MS and LA-ICP-TOF-MS will be discussed.

Using pneumatic nebulization and microdroplet generation, we have also studied the up-take of nanoparticles and toxic metals as well as essential elements time resolved in single cells using different mass spectrometric concepts (sector field, triple-quad, time of flight (TOFWERK) and mass cytometry (CyTOF)). Calibration was performed by application of nanoparticle suspensions. The different ICP-MS based methods will be compared concerning their analytical figures of merit and their strengths and weaknesses will be evaluated.

All examples clearly demonstrate that ICP-MS can be successfully applied to study metals and metallic nanoparticles in single cells.

Keywords: Single cell analysis, laser ablation, ICP-SF-MS, ICP-TOF-MS, ICP-MS/MS

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PLF-2 Exploring the Earth with MC-ICP-MS

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In the last 20 years, stable and radiogenic isotope research has enormously benefited from the advent of Multi Collection – Inductively Coupled Plasma – Mass Spectrometry (MC-ICP-MS). These instruments permitted to explore the natural ranges of the stable isotope composition of elements like iron, copper or titanium, otherwise difficult to measure precisely and accurately with more conventional analytical techniques such as Thermal Ionisation Mass Spectrometry (TIMS) or gas source mass spectrometry. As a result, we now have an improved knowledge of the stable isotope systematics of these elements in rocky and aqueous terrestrial reservoirs and, more recently, biological samples.

However, most of these studies were conducted on "bulk sample" determinations obtained after purification by wet chemistry and solution analysis by MC-ICP-MS. Although useful for the big picture and global models based on mass balance and flux calculations, a large part of the potentially useful isotopic information, locked within the studied samples, is overlooked with this approach.

For instance iron isotope determinations of "bulk" riverine samples are useful to yield estimates of the origin and pathway of the iron carried by waters and to produce chemical mass balance estimates at the river basin scale. However, filtration experiments, provided they are unbiased, reveal that the stable isotope systematic of the different water fractions provide an original insight. Combined with other physical and chemical characterization techniques, it can yield a detailed insight into the iron cycling in natural waters with potential global environmental outcomes.

Similarly, iron and silicon isotope determinations based on rock powders provide hints on the composition of deep planetary reservoirs or on terrestrial planets accretion modes. However, for rare and small samples, such as the Apollo lunar rocks, a sample size issue may arise. For these and other terrestrial bulk rocks, some isotopic variations cannot sometimes be simply explained. In such cases, the in situ, stable isotopic analysis of the rock mineral constituents is required. This is performed through developments such as laser ablation MC-ICP-MS, although precise and accurate measurements remain challenging.

Hence, time is ripe for the development of hyphenated techniques allowing in situ isotopic analyses of solids, or compound specific isotopic analyses of aqueous and biological samples to go one step further into our understanding of nature based on stable metal isotope investigations.

Keywords: isotope geochemistry, rock, mineral, river, water

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OF-01 Trace element profiling in very small volumes of human serum for the application in large cohorts.

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Trace elements (TE) play an important role for general health and wellbeing in the human body. They are a vital part of multiple enzymes, hormones and transmitters and thus need to be adequately supplied via nutritional intake. There are multiple studies on changing TE-homeostasis during aging, due to both pathologic, and natural changes. However, in most studies, the focus lies on a single or sometimes two elements. Interactions of multiple elements at the same time are rarely investigated, although most bodily functions depend on several TE.

This issue is addressed by the DFG research unit #2558 TraceAge. We aim to investigate the interactions and status of six TE, namely manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), selenium (Se) and iodine (I). Therefore we analyze TE-profiles in large cohorts, such as the EPIC- Potsdam cohort, investigate the effects of TE-adequate and subadequate conditions in *in vivo* models like *M. musculus* and *C. elegans*, and attempt to establish novel biomarkers for the determination of i.e. oxidative stress and DNA-damage caused by the disruption of the TE-homeostasis. Hereby, the focus lies on age-related changes.

Every large human cohort has one major limitation, which is the amount of sample material available. Most of the time, only a few microliters of i.e. serum are available for a single purpose like TE-profiling. This limits the number of measurable analytes and/or endpoints significantly. For this study, we adopted an ICP-MS/MS method published by Konz *et al.* for an amount of 500 µL of serum and measurement of 33 elements simultaneously. Instead of digesting, the sample is diluted using a special diluent containing EDTA, butanol, ammonia and surfactant. We miniaturized this method for the measurement of 6 elements in as little as 50 µL of serum. The modified method was validated against serum reference materials and compared to a conventional acid-digestion method and found to be in excellent agreement. The achieved detection and quantification limits are sufficient for the concentrations that are expected in human serum from central European study participants. Furthermore, the use of an alkaline diluent allows for simultaneous measurement of iodine, which is not possible in acidic conditions.

After validation, the method has been applied to samples from the EPIC-Potsdam cohort, as well as to murine samples from the TraceAge animal experiments. The method proved to give reliable results for both species. This allows for the comparison of TE-profiles in multiple species, which is important for the validation and applicability of animal models in relation to human health.

Keywords: trace elements, ICPMS/MS, TraceAge, serum, cohort, aging, isotope dilution

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OF-02 Nanoplastics, the new threat to our environmental waters: how can ICP-MS help us to address this issue?

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In contemporary society, plastics have achieved a pivotal status, with extensive commercial, industrial and medicinal applications. Through accidental release and indiscriminate discards, plastic wastes have been accumulated in the environment at an uncontrollable rate **[1]**, having been detected in the oceans, soils, sediments and surface waters worldwide. A recent paper in *Science* estimates the total amount of plastic debris landing in the oceans at about eight million metric tons **[2]**. A lot of studies have shown that, once in the marine environment, plastics can be degraded into smaller debris like microplastics. However, the amount of microplastics observed in oceans is far from what is expected, and hence the plastic pollution is still far from being well understood. There is more and more evidence that supports the hypothesis that the fragmentation process finally leads to submicronic fragments, that is, nanoplastics, which cannot be detected so far. In this context, the European Union has alerted about the insufficient data on the occurrence, toxicity and fate of micro- and nanoplastics, pointing out that nanoplastics require special attention **[3]**. In addition, nanoplastics, due to their high surface to area ratio can act as concentrators and carriers of other pollutants present in the environment like heavy metals, changing the paradigm of environmental pollution in waters.

However, this presentation will show how analytical chemistry, with the development of novel and innovative strategies based on the use ICP-MS techniques, in combination with polymer science (synthesis of model nanoplastics) and physico-chemical characterization, can provide new knowledge about the occurrence of nanoplastics and their interaction with toxic metals. The synthesis of nanoplastics standards representative of environmental proved to be good models for the development of a multidimensional analytical approach (based on the combination of asymmetrical flow field-flow fractionation (AF4) coupled to ICP-MS, and single particle ICP-MS) to detect and quantify nanoplastics through metal labelling. This novel strategy, applied to models and real samples and in combination with a physico-chemical characterization of nanoplastics can shed light about the role of nanoplastics as vectors of concentrated environmental pollution and the Trojan horse effect mechanism.

Keywords: nanoplastics, single particle ICP-MS, environment, pollution

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OF-03 Study on speciation of As, Cr and Sb in bottled flavored and functional drinking water samples using advanced analytical techniques IEC-SEC-HPLC-ICP- DRC-MS and ESI-MS

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Water is among the most basic elements of human diet and it is essential for sustaining life and good health. Consumption of bottled drinking water is constantly growing in recent years and current projections indicate that it is likely to become the most consumed beverage type. Beyond mineral water, soft drinks such as flavored and functional bottled drinking waters have shown growing consumption over the recent years. It is known that the bottles can release harmful elements such as arsenic, antimony or chromium into drinking water. The presence of various additives in bottled flavored and functional drinking waters may result in a presence of greater variety of As, Cr and Sb species (including organic forms) in those samples than in mineral waters. It is well known that the effect of As, Cr and Sb on human health depends not only on the dose or route of administration but also on the chemical form in which these elements occur. For both arsenic and antimony, their trivalent species are much more toxic than pentavalent. Also, As and Sb inorganic compounds has been classified as a human carcinogen same as Cr(VI). In opposition to hexavalent chromium, Cr(III) does not exhibit any adverse effects on the human body. Complex organic compounds of As and Sb are notably less harmful to humans. For all of the above reasons, a quality control of bottled drinking water requires to determine concentration of high variety of both inorganic and organic As, Sb and Cr species **[1]**.

In the present work, two advanced analytical techniques have been employed to study speciation of As, Cr and Sb in bottled flavored and functional drinking water samples. High performance liquid chromatography coupled with inductively coupled plasma mass spectrometry equipped with dynamic reaction cell (HPLC-ICP-DRC-MS) was used in combination with two chromatographic methods, size exclusion chromatography (SEC) and ion exchange chromatography (IEC). The use of two chromatographic methods with ICP-MS detection allowed the determination of both inorganic and organic compounds of the above-mentioned elements in the test samples. In order to identify the detected organic forms of As, Cr and Sb, high resolution mass spectrometry with electrospray ionization (ESI-MSn) has been applied. The quality control of the obtained results has been achieved through the analytical validation, assuring of measurement traceability and estimation of the measurements results uncertainty. Four analytical procedures have been employed: Procedure 1 – multielemental speciation analysis of: As(III), As(V), Sb(III), Sb(V) and Cr(VI) using IEC-ICP-DRC-MS; Procedure 2 – speciation analysis of: AsB, As(III), DMA, MMA and As(V) using IEC-ICP-DRC-MS; Procedure 3 - multielemental speciation analysis of As, Cr and Sb using SEC-ICP-DRC-MS; Procedure 4 – identification of detected organic species using ESI-MSn. The obtained results were compared with the results obtained in earlier studies for bottled mineral waters **[2]**.

As(III) and As(V) were found in bottled mineral, flavored and functional waters. Sb(V) and Cr(VI) have been found only in mineral waters. Sb(III), MMA and DMA have not been detected in any of the analyzed samples. AsB and Cr(III) have been found in bottled flavored and functional drinking water samples only. Results obtained from SEC-ICP-DRC-MS analysis show presence of As, Cr and Sb species with various molecular masses. Use of ESI-MSn allowed for confirming the presence of some organic compounds containing arsenic. The validation of the analytical procedures confirmed that the procedures provide reliable results.

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Keywords: speciation, bottled drinking water, HPLC-ICP-DRC-MS, ESI-MS, validation, As, Cr, Sb

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OF-04 Determination of sulfur containing compounds in crude oil products by GC-ICP-MS/MS

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Crude oil consists of a complex matrix containing a large variety of organic molecules, including S-, N- and O-containing compounds. The content of sulfur in crude oil can represent up to 10%. Sulfur compounds include thiols, sulfides and aromatic sulfur heterocycles. Therefore, their determination is important both for assessing the product quality of crude oil derivates but also for the characterization of future environmental emissions derived from their use.

Considering the wide variety of S-containing compounds present in fuel samples, generic quantification without specific standards would be desirable. To the best of our knowledge, compound independent calibration (CIC) in real samples has only been achieved so far by post- column isotope dilution and GC-ICP-MS **[1]**. However, this method requires the synthesis and the continuous addition of a ^{34}S-labelled gaseous compound flow which hampers it use in routine analysis.

In this communication, we present a GC-ICP-MS/MS approach for the absolute quantification of sulfur compounds in crude oil products using a simple and certified generic S- containing standard. In an initial step, the conditions for the acquisition of the sulfur signal by the GC-ICP-MS/MS were optimized. Then, experimental conditions leading to CIC (full recovery from the GC injector and column) were evaluated and optimized with different S-containing standards. Finally, influence of the co-elution with other massive matrix (oil) components was assessed as well.

Under optimized working conditions, detection limits as low as 5 ppb were obtained. CIC method was validated by analysis of the certified reference material ERM-EF213 ("sulfur free gasoline" with 9 ppm of total sulfur content).

Finally, the optimized approach was successfully applied to real samples, diesel and gasolines.

Keywords: S, containing compounds, crude oil products, GC-ICP-MS/MS, absolute quantification, certified generic S, containing standard, compound independent calibration

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OF-05 Hyphenation between capillary electrophoresis and multi collector inductively coupled plasma mass spectrometry for isotope ratio measurements

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Determination of precise isotope ratio is of major concern in the nuclear industry for validation and qualification of neutronic calculation code, waste management, safeguards or nuclear forensics. Nuclear samples display complex matrices leading both spectral and non-spectral interferences among radionuclides. Their elimination is mandatory to obtain accurate isotope ratio measurements and, in most cases, isotope ratios are determined off-line after well-established chemical separation steps which are generally time and solvent consuming. Various analytical developments are performed at the Nuclear, Isotopic and Elementary Analytical development Laboratory (LANIE) at CEA Saclay with the goal to reduce the amounts of samples required, the handling time on radioactive samples and the radioactive wastes produced. Since electrokinetic methods only involve ions migration under the influence of an electric field, they enable a significant reduction of liquid waste as well as sample consumption which is in the nano- or microliter range. Furthermore electrokinetic techniques can be now easily coupled to the ICP source of a mass spectrometer. We will present a new analytical approach based on capillary electrophoresis (CE) hyphenated to MC-ICP-MS for U and Pu isotope ratios determination in nuclear fuel sample within a single analytical run. The separation was performed with only few nL of a solution of spent nuclear fuel using acetic acid as electrolyte and after an oxidation step in order to maintain Pu in a same valence state. We will focus this presentation on the analytical strategy to perform mass bias correction during the separation and the data treatment methods used to evaluate isotope ratio on transient signals. Analytical performances and the advantages of this approach for nuclear topics will be discussed.

Keywords: MC-ICP-MS, hyphenation capillary electrophoresis and MC-ICPMS, transient signals

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OF-06 Headspace analysis of Hg in petroleum hydrocarbons

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Traditional methods for mercury (Hg) speciation in petroleum hydrocarbon matrices by gas chromatography (GC) entail injection of derivatised liquid samples, which very often significantly reduces the lifetime of chromatographic columns. To minimize the negative impact on the column, samples can be diluted. However, doing so, the trace levels of Hg often fall below the limits of detection and there are no good online preconcentration techniques when it comes to analytes in organic matrices. We developed an accurate and sensitive method for determination of Hg species in PHs by headspace sampling with a possibility of on-line pre-concentration using in-tube extraction (ITEX) combined by GC-ICP-MS analysis. Mercury species were first extracted from the PHs matrix into aqueous phase via dithizone chelation and subsequently converted with sodium tetrapropyl borate into volatile derivatives which could be sampled from the headspace prior to GC- ICP-MS analysis. For concentrations in ng.kg^{-1} range on-line ITEX method was applied whereas g.kg^{-1} range was accessible by static headspace. Quantitation of Hg species was carried out by double isotope dilution method with quantitative recoveries of monomethyl Hg (MMeHg) (average
101 5%) and inorganic Hg (InHg) (average 97 7%) by direct headspace injection. Average recoveries of Hg spikes after on-line ITEX pre-concentration were 95 3% for MMeHg and 98 8% for InHg. The detection limits for MeHg and InHg were 428 and 46 ng.kg^{-1} when measured by static headspace, 2.4 ng. kg^{-1} and 1.7 ng.kg^{-1} by on-line ITEX pre-concentration. Accuracy of the pre- concentration method was demonstrated by analysis of crude oil standard reference material (NIST 2722) certified for InHg.

Keywords: Hg speciation, crude oil, GC-ICP-MS

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OF-07 The use of hyphenated techniques (CZE-ICP- MS, HPLC-ICP-OES) for the study of inorganic complexes

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It is known that the chemistry of the complex compounds is a high-growth area of modern inorganic chemistry. For instance, polynuclear complexes (PNCs) of Rh(III) were found to be promising catalysts in organic synthesis **[1]**. The preferable way to prepare such catalyst is the precipitation of rhodium (III) hydroxide to the surface of oxide carrier in an alkali solution. Under these conditions, rhodium (III) hydroxocomplexes are capable of polycondensation, forming a variety of polynuclear hydroxobridged species with {Rh(-OH)Rh} fragment.

Evidently, catalytic activity is strongly dependent on a catalyst composition, thus, as the resulting mixture is not represented by an individual compounds, it is necessary to understand what polynuclear species of rhodium are formed in an alkali solution. To clarify this question, the separation techniques such as capillary electrophoresis (CE) and high performance liquid chromatography (HPLC) coupled with an element-selective detector seem to be the most promising approaches. The goal of the present work was to separate and identify mono- and polynuclear species using these techniques.

There are a number of problems in the study of such compounds: the absence of individual compounds with known polymerization number, similar UV-Vis absorption spectra for polynuclear complexes with different polymerization number and limited range of stability of complexes. Recently, we reported the first application of coupled HPLC-ICP-OES in the chemistry of polyoxometalates – complexes with similar set of problems as PNC has. This technique proved very efficient for the study of the mixtures formed in self-assembly reactions of inorganic complexes **[2]**.

The generation of a number of different Rh(III) species, which include bi- and tridentate and etc. OH-ligand bridging, CZE-ICP-MS and HPLC-ICP-OES were applied. As a result, the approaches for the study of the mixtures formed in the process of rhodium polynuclear forms generation were developed. It was shown that CE and HPLC might be successfully applied for the study of the state of inorganic complexes in solution. However, the most appropriate approach for the study of these mixtures is the combination of different techniques such as HPLC, CE, UV-VIS and corresponding hyphenated techniques.

Keywords: hyphenated techniques, CZE-ICP-MS, HPLC-ICP-OES, inorganic complex, rhodium

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OF-08 Speciation of trace contaminants in the refinery industry using gas chromatography coupled to ICP-MS/ MS

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The nature of contaminants in petroleum products depends on the crude oil origin, refining process and agents added during refining steps **[1]**. Most of them (As, Cl, Si, Hg, Ni, V, etc.) are known to severely poison catalysts **[2]**. These elements are present at trace levels typically ranging from several $g.kg^{-1}$ to several $mg.kg^{-1}$, depending on the boiling point (ranges) of the petroleum cut and on the element. To avoid catalysts poisoning and to cope with the specifications of the different commercial fuels, these elements must be removed using trapping systems. Development and optimization of these systems require the determination of the total elemental concentration as well as their speciation.

Total content determination in fuels and biofuels is usually carried out using atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) **[3]**. To perform elemental speciation, separation techniques hyphenated to either mass spectrometry or ICP-MS have been proposed **[4]**. However, some elements, (^{35}Cl, ^{28}Si...) are difficult to analyse and especially in organic matrices because of interferences at low masses. Recently, inductively coupled plasma tandem mass spectrometry (ICP- MS/MS) was considered to be a versatile tool for the study of interfered elements at trace levels in very complex matrices such as petroleum products.

In this presentation, speciation of various contaminants (As, Cl and Si) in petroleum products are reported using the ICP-MS/MS 8800 Agilent system. Results concerning the optimization of carrier, auxiliary gas and collision reaction cell (CRC) with different gases (H_2, O_2, ...) to limit interferences are presented in terms of sensitivity and robustness. The application of GC-ICP-MS/MS to gasoline cuts coming from various refining processes is then discussed.

Keywords: speciation, petroleum products, refinery, trace, interferences, gas chromatography, ICP-MS/MS

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OF-09 Arsenic speciation analysis in liquid and solid samples by hyphenated technique HPLC-ICP-DRC-MS

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Speciation analysis of arsenic in liquid and solid samples, environmental, biological as well as food ones is a subject of research of many scientists. It is well known that only some of the arsenic species are toxic, the highest toxicity demonstrate inorganic arsenic compounds, the lowest toxicity demonstrate organic compounds, such as arsenobetaine and arsenocholine **[1]**. Therefore, determination of only total concentration/content of arsenic is insufficient to assess the effect of the arsenic on the environment or human organism. Presence of arsenic in the environment, especially in groundwater used as a source of drinking water, is an issue of great importance because of the serious health consequences. Determination of arsenic concentration in other types of water is essential for evaluation of environmental pollution **[2]**. In reference to food, its consumption when contains arsenic compounds can cause a significant increase in exposure to toxic arsenic species. Hence the great need to conduct speciation analysis of arsenic in food samples in order to determine the biotoxicity and bioaccumulation of this element.

The aim of our research was to develop analytical procedures dedicated to: i) total arsenic determination in water and freshwater fish samples using inductively coupled plasma mass spectrometry with dynamic reaction cell (ICP-DRC-MS) ii) arsenic speciation analysis of As(III), As(V), DMA, MMA and AsB in water samples using high performance liquid chromatography coupled with ICP-DRC-MS [3]; iii) arsenic speciation analysis of As(III), As(V), DMA, MMA and AsB in freshwater fish samples by HPLC-ICP-DRC-MS. This process consisted of some important steps: i) optimization of ICP-MS working parameters and DRC; ii) optimization of HPLC separation parameters; iii) optimization of digestion and extraction procedures by microwave digestion system EthosOne in case of solid samples; iv) validation of procedures according to metrological approach using certified reference materials such as River Water SLRS-5, Tuna Fish Tissue BCR 627, Fish Muscle ERM-BB422. Developed and validated analytical procedures were applied to the real samples of different types of water and freshwater fish. Results demonstrated high arsenic concentration reaching even 3800 $g.L^{-1}$ (in the form of As(V)) in surface water from the Lower Silesia province. Fish samples from Lower Silesia province contained significantly more arsenic than fish sampled in Wielkopolska province. AsB predominated in all samples, trace amounts of As(V) were found in fish from Lower Silesia province.

The research was carried out using a liquid chromatograph (PerkinElmer Sciex, Canada) together with Hamilton's anion exchange column PRP-X100, and an ICP-MS spectrometer model ELAN DRC II with a dynamic reaction cell (PerkinElmer Sciex, Canada).

Keywords: arsenic, speciation, high performance liquid chromatography, inductively coupled plasma mass spectrometry

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OF-10 Application of single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) in the petroleum industry

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has emerged as a powerful tool to characterize nano/submicronic particles in different matrices. In this study, we used SP-ICP-MS to answer nanoparticle questions in real-world samples that traditionally use TEM, SEM or NTA for size characterization. For this petroleum application, the particle size determination of nano/submicronic catalyst precursors dispersed in heavy oil fractions was measured. The fact that samples can be diluted in organic solvents and the resultant solution can be introduced directly into the instrument, make this technique very appealing for various applications. Here, we present the application of this technique on the particle size characterization of i) nano/submicronic catalysts precursors dispersed in different heavy oil media; ii) iron particles present in hydrocarbons iii) native particles present in crude oil. Plasma stability in hydrocarbon media, nebulization efficiency and interference removal were evaluated. Results obtained by SP-ICP-MS were compared to other techniques routinely used for nanoparticle characterization.

Keywords: single particle ICP-MS, nanoparticles, submicronic particles, petroleum

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CEM Corporation is the world leader in microwave sample preparation for ICP-OES and ICP-MS. The industry leading MARS 6 microwave digestion system brings unparalleled simplicity to trace metals sample preparation. MARS 6 is the perfect solution for labs digesting large number of samples a day as it can digest up to 40 samples in a single batch. It is also the perfect tool for digestion of difficult samples using the new iPrep vessel which can reach temperatures of up to 300 ˚C to completely solubilize challenging inorganic matrices. With the precise control of iWave, contactless in-situ temperature measurement, the MARS 6 is the safest and easiest-to-use microwave digestion system available.
We continue to innovate new products and accessories to solve a wide variety of applications from speciation to the most difficult sample matrices. Our latest innovation, the Discover SP-D Clinical focuses on an underserved market that requires microwave systems to work with very small sample sizes and volumes. The small cavity of the Clinical is designed specifically for these sample types and the accompanying 4 and 10 mL sample vials can work with volumes as low as 500 µL.
www.cem.com

Courtage Analyses Services. For more than 20 years we are the specialist in sample preparation, digestion and introduction for metal analysis by ICP, ICP-MS, AAS, IC etc. thanks to our skill, we became official dealer, mostly in France, European and African French speaking countries of leading designer and producer companies like

• GLASS EXPANSION with nebulizer, spray chamber, torch and cones. holder of several patents and owner of the registered trademarks like SeaSpray, Vitricon, D-Torch, TruFlo, IsoMist Eluo ect…

• SAVILLEX with PFA labware, acids distillers, graphite heating plate, sample introduction system, necessary for all ultra traces metal analysis by ICP/MS and ICP-IR/MS, the most efficient distillers on the market will allow you to obtain the purest acids while achieving significant savings for your laboratory

• BERGHOF with Hight-pressure vessels and microwave digestion. Holder of 4 patents the Speedwave XPERT can digest samples impossible with competition All µ-wave digestion vessels got a 3 years warranty.

• ANALYTIKA European CRM standard solutions producer by primary method design offering also RM standard and custom blend solutions, ultra-pure acids and solid pure material if you want to prepare yourself your standard.

• ENVIRONMENTAL EXPRESS with sample digestion in PP tubes in graphite HotBlock,

• PHOTRON with hollow cathode lamp for AAS

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For laboratories also involved in Isotope Ratio measurement, we also offer a range of consumables CHNOS and EA-IR-MS instruments from all brands.

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Elemental Scientific designs and produces a full range of automation, online monitoring and sample introduction systems for the determination of trace element concentrations in liquid. Our extensive portfolio contains sample introduction devices for all models of ICPMS, ICPAES and ICPOES instruments. Elemental Scientific also provides complete sample introduction kits for specific trace metal and non-metal applications, including semiconductor pure chemicals, environmental, clinical, organic solvents, isotope ratio, and many other types of trace metal determinations. www.ICPMS.com

Elemental Scientific Lasers has a range of products to meet the diverse needs of ICP-MS users and the vastly different applications that they perform. From the NWR266macro designed with industrial bulk analysis in mind, to the NWRimage with its sub 1 micron laser spot designed for bioimaging at the cellular level, Elemental Scientific Lasers has a solution to meet your requirements.
www.NWRLasers.com

MEINHARD® is the partner of choice for many of the world's plasma spectroscopy instrument manufacturers. As a leading manufacturer and global supplier of high precision nebulizers and scientific glassware; our clients demand the highest levels of design, manufacturing, delivery, and customer service. For over 40 years MEINHARD® has had a rich legacy of meeting critical requirements ranging from applications that require high sensitivity to the fastest throughput, MEINHARD® can supply products for all ICP and ICPMS needs. www.Meinhard.com

HORIBA Scientific, part of HORIBA Instruments, Inc., headquartered in the United States, provides an extensive array of instruments and solutions for applications across a broad range of scientific R&D and QC measurements. HORIBA Scientific is a world leader in OEM Spectroscopy, elemental analysis, fluorescence (including the PTI brand), forensics, GDS, ICP, particle characterization, Raman, spectroscopic ellipsometry, sulphur-in-oil, water quality, SPRi and XRF. Our instruments are found in universities and industries around the world. Proven quality and trusted performance have established widespread confidence in the HORIBA Brand.

Building on a long tradition of pursuing innovative technology to advance scientific efforts, we have acquired renowned companies such as Société Générale d'Optique (1969), SPEX (1988), Dilor (1995), SOFIE (1996), Jobin Yvon (1997), IBH (2003), GenOptics (2009), and Photon Technology International (2014).

The HORIBA Group of worldwide companies, part of HORIBA, Ltd. headquartered in Kyoto, Japan, provides an extensive array of instruments and systems for applications ranging from automotive R&D, process and environmental monitoring, in-vitro medical diagnostics, semiconductor manufacturing and metrology, to a broad range of scientific R&D and QC measurements.
Web site : horiba.com/scientific

Kashiyama. In the design and manufacturing fields of vacuum pumps for Semiconductor and FPD manufacturers, our core business, we continue to maintain No.1 market share within the Japanese market. The primary focus of our customer-oriented approach is to gain a full understanding of our customers' requirements to provide suitable products on-time.
With the founding of Kashiyama Europe GmbH in 2018, Kashiyama Industries Ltd wishes meet the requirements of the European market and respond to the increasingly complex needs of the customers with creative solutions.
Our main business is the development and manufacturing of oil-free dry vacuum pumps as energy saving, low maintenance multistage, roots pumps. The focus of our approach is to support our customers with optimal technology for their different usages in the semi-conductor technique, analytical or branch-specific vacuum equipment, as well as R&D.
Based on the concept of «Total Cost of Ownership», we are proud to serve our customers in every stage from design to maintenance for their daily business activities, to meet their needs and to support with our yearlong experience as one of the market leaders. To this purpose, we have our worldwide service-network.

Labkings. At LabKings we provide high quality products (100% compatibility), with an excelent level of service to the laboratory community. We service or valued customers with a one-stop-shop experience combined with the best communication possible, reliable on-time delivery and a high quality standard.
LabKings is a specialist in ICP & ICP-MS consumables and has access to all major manufacturers in the Analaytical Chemistry industry.
We supply:
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LabKings provides certified standard solutions for both Inorganics ICP, ICP-MS and Organics -GC, GC-MS, HPLC use. Our NIST traceable standard solutions are produced by an accredited laboratory according to ISO / IEC 17025 / Guide 34 (A2LA). Quality systems of the manufacturer is tested by NSF-ISR ISO registered (9001: 2008). All our standard solutions are provided with a Certificate of Analysis (CofA) & Safety Data Sheet (SDS) documentation. Labkings also offers Custom Made Solutions.

Please feel free to browse our site (www.labkings.com) to get a better understanding of our products and services and to purchase products or to contact us for a quote (info@labkings.com). For our availability in stock you can contact the LabKings team at: +31-35-2400142 or via the mail.
We are happy to assist you.
We love to meet you at our booth in Pau opposite the catering lane. We welcome you with a glass of wine complementary to our Dutch cheese. We also have our mascotte Professor Elementius T-shirts and USB sticks to remember us by. You are very welcome!

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At Milestone, we help chemists providing the most innovative technology for sample
preparation and direct mercury analysis. Milestone has been active since 1988 in the
field of advanced sample preparation. We are the acknowledged industry leader in microwave instrumentation technology holding over 50 patents and more than 20.000 sample preparation instruments installed worldwide covering government, academic, contract, and manufacturing industries. Our industry-leading technology on sample preparation for trace metal analysis and organic contaminants, in combination with fast,
responsive service and applications support, allows Milestone to provide great ownership experience. Milestone offers industry-leading solutions for Microwave Digestion for AA, ICP and ICP-MS analysis, Microwave Extraction, Acid Purification, Direct Mercury Analysis, Microwave-Assisted Synthesis and Microwave Ashing. Milestone is headquartered in Italy and has offices in Germany, Switzerland, the Unites States, China, Japan and Korea; Milestone operates worldwide through a network of over 100 exclusive factory-trained distributors.

PerkinElmer – The Most Trusted Name in Elemental Analysis
With about 11,000 employees serving over 150 countries, PerkinElmer is a $2.3 billion global leader committed to innovating for a healthier world. We are passionate about providing customers with an unmatched experience as they help solve critical issues especially impacting the diagnostics, discovery and analytical solutions markets. PerkinElmer has been at the forefront of inorganic analytical technology for over 50 years. With a comprehensive product line that includes the most powerful ICP-MS systems, flexible ICP-OES systems, high-performance Graphite Furnace AA systems and Flame AA systems, we can provide the ideal solution no matter what the specifics of your application.
We understand the unique and varied needs of the customers and markets we serve. And we provide integrated solutions that streamline and simplify the entire process from sample handling and analysis to the communication of test results.
With tens of thousands of installations worldwide, PerkinElmer systems are performing inorganic analyses every hour of every day. Behind that extensive network of products stands the industry's largest and most-responsive technical service and support staff. Factory-trained and located in 150 countries, they have earned a reputation for consistently delivering the highest levels of personalized, responsive service in the industry.

Postnova, founded in 1997 as a Spin-Off from Technical University Munich and now located in Landsberg am Lech, Germany with subsidiaries in Salt Lake City, USA and Malvern, UK, is the leading manufacturer of analytical instruments based on the principle of Field-Flow Fractionation (FFF). With an application range of 1 nm to 100 µm and 1000 Da up to several MDa, FFF is indisputably one of the most potent and flexible analytical tools for the fractionation of organic and inorganic nano- and microparticles as well as synthetic and biological polymers, proteins, viruses, antibodies, liposomes or exosomes both in complex aqueous and organic matrices. To cover these various applications, Postnova provides the complete range of FFF instrumentation including Asymmetrical Flow FFF, Electrical Asymmetrical Flow FFF, Centrifugal FFF, Thermal FFF and Gravitational SPLITT along with sophisticated detection systems such as e.g., UV-vis Spectroscopy (PN3200 UV), Multi-Angle Light Scattering (PN3600 MALS), Dynamic Light Scattering (e.g. Malvern Zetasizer), Intrinsic Viscosity (PN3300 Visco), Refractive Index (PN3100 RI) and Inductively-Coupled Plasma Mass Spectrometry (e.g. Agilent 7900 ICP-MS). With this modular approach that combines high-resolution fractionation with powerful detection; Postnova offers a comprehensive characterization platform that can be tailored to your needs to solve your analytical challenges.

RADOM architects a new frontier in instrumentation to bring a robust plasma source to the field of analytical spectroscopy. Radom offers the MICAP plasma source that maybe coupled to both OES and MS detection instruments. By allowing standard sample introduction, standard glassware, and offering throughput specfications equivalent to typical ICP, the MICAP plasma source is available to be coupled to any MS instrument in a modular fashion. The N2 -MICAP source provides a much “cleaner” background spectrum than the ICP; absence of argon-based interferences greatly simplifies analysis of isotopes such as 40 Ca, 56 Fe, and 75 As, which typically suffer from spectral interferences in ICP-MS. The major plasma species measured from the N2 -MICAP source include NO^+ , N_2^+ , N^+ , N_3^+ , O_2^+ , N_4^+ , and H_2O^+ ; and there are no observed plasma-background species above mass-to-charge 60. Absence of troublesome argon-based spectral interferences is a compelling advantage of the MICAP source. For example, with MICAP-TOFMS, the limit of detection for arsenic is less than 100 ng L^{-1} even in a 1% NaCl solution; with ICP-MS, $^{35}Cl^{40}Ar^+$ interferes with $^{75}As^+$ and arsenic analysis is difficult-to-impossible in chlorine-containing matrice [Anal. Chem. 2018,90,22,13443-13450].
If you are interested in advancing your research in Laser Ablation, Speciation, Complex matrices and others, without the interferences of Argon while achieving high detection limits please contact sales@radomcorp.com

The Royal Society of Chemistry is the world's leading chemistry community, advancing excellence in the chemical sciences. With over 50,000 members and a knowledge business that spans the globe, we are the UK's professional body for chemical scientists, supporting and representing our members and bringing together chemical scientists from all over the world.
A not-for-profit organisation with a heritage that spans 175 years, we have an ambitious international vision for the future. Around the world, we invest in educating future generations of scientists. We raise and maintain standards. We partner with industry and academia, promoting collaboration and innovation. We advise governments on policy. And we promote the talent, information and ideas that lead to great advances in science.
In a complex and changing world, chemistry and the chemical sciences are essential. They are vital in our everyday lives and will be vital in helping the world respond to some of its biggest challenges.
We're working to shape the future of the chemical sciences – for the benefit of science and humanity.

Savillex provides a full range of PFA labware products and technologies designed to minimize contamination and maximize data quality for trace metals analysis. Our jars, vials, bottles, and digestion vessels are all produced from virgin, high-purity PFA resin and offered in various shapes and sizes. Savillex's market-leading DST Series of acid purification systems have given thousands of analytical labs around the world the ability to produce their own ultra, high-purity acid (10 ppt) resulting in significant cost savings and dependable acid quality.
Recently, Savillex introduced the HPX Series of PFA-coated inert hotplates which help diminish contamination during sample prep and also maximize hotplate longevity by virtually eliminating system corrosion. When it finally comes to analysis, Savillex optimizes your ICP-OES and ICP-MS by offering a complete line of PFA sample introduction systems.
When your applications demand the lowest levels of detection, Savillex has a solution that meets your needs.

Shimadzu. Instruments and solutions at top level reliability and performance
Shimadzu as a worldwide leading manufacturer of analytical instrumentation provides essential tools for quality control of consumer goods and articles of daily use, in food, beverages and agriculture as well as in all areas of environmental and consumer protection. Since more than 140 years, Shimadzu has been at the service of science ensuring precise, reliable diagnoses and analyses in food, chemistry, pharmacy and medicine. Shimadzu´s innovative solutions in field of atomic- and molecular spectroscopy, chromatography, mass spectrometry and material testing ensure the highest level of reliability and performance.
Shimadzu's Inductively Coupled Plasma Mass Spectrometer ICPMS-2030 supports an extensive range of analysis from trace levels to high concentrations. It is ideal for the elemental analysis of sample solutions, in particular where the lowest detection limits are demanded. The system configuration includes a user-friendly software package with two "assistant" functions to simplify analysis. The spectrometer is designed for high stability, high sensitivity and low interferences. The unique energy saving features such as the patented minitorch developed by Shimadzu resulting in low running costs.

Spectroscopy magazine. For the past 33 years, Spectroscopy's mission has been to enhance the productivity, efficiency, and the overall value of spectroscopy as a practical analytical technology across a variety of fields. Scientists, technicians, and laboratory managers gain proficiency and competitive advantage for the real-world issues they face through unbiased, peer-reviewed technical articles, trusted troubleshooting advice, and best practices application solutions. Spectroscopy is indexed in the Science Citation Index, Web of Science: Science Citation Index Expanded, Journal Citation Reports, and EBSCOhost.

Spectron. Since 1988, Spectron, Inc. has been manufacturing and supplying quality cones and consumables to the ICP & ICP-MS community worldwide. With extensive experience in ICP-MS and ICP-OES techniques, we bring a unique level of expertise to the manufacturing process. Developing Partnerships with companies like Agilent Technologies and others, Spectron is continually improving and updating our techniques and processes, keeping up with the critical demands of our growing industry. Spectron manufactures sampler and skimmer cones for all the major brands of ICP mass spectrometers including Agilent, GBC, MicroMass/GV, Nu Instruments, PerkinElmer and Thermo Fisher. We offer our customers the highest quality consumables and accessories available anywhere. Through our website and with the aid of local dealers, our products and services are available around the globe. Spectron stands behind all the products we sell. Whether sample cones, glassware, detectors or accessories, we are committed to the highest level of customer satisfaction and support. Our experienced engineers and state-of-the-art equipment enable us to help bring your concepts through the design, prototype, and final production stages. If you desire, we are strategically configured to scale up rapidly, as your business grows, keeping pace with your needs.

Spetec GmbH, founded in1987 and located in Erding, Germany, is the leading supplier of peristaltic pumps. Spetec engineering offers products for the modern laboratory, such as a comprehensive selection of various tubing made to meet the most stringent specifications for peristaltic and syringe pumps. Thanks to the highest quality and precision, Spetec became the leading supplier of peristaltic pumps. A comprehensive selection of various tubing types for their application is offered as well. Over the years, Spetec has also developed a broad range of clean room solutions. Today Spetec delivers individual clean room solutions ranging from the mobile Laminar Flow Box to complex, turnkey clean room systems. Spetec also offers the maintenance and certification of clean room systems according to DIN ISO.
Based on many years of experience in clean room technology, the area of laser safety business has emerged. Individual laser safety systems are offered according to customer requirements. Innovative, application-oriented products are created through the combination of in-house development, design and fabrication centralised under one roof.
Spetec provides customized products that can be tailored to your needs and specifications.

SPEX Europe is the European division of SPEX CertiPrep Group representing SPEX CertiPrep, SPEX SamplePrep and Katanax throughout the EMEA region. We manufacture Certified Reference Materials for AA, IC, ICP, ICP-MS, GC, GC-MS, HPLC, LC-MS. We offer custom made solutions based on your lab's individual needs.
We also provide superior laboratory equipment such as cryogenic mills, presses and fusion fluxers that have become the industry standard for reliability and durability being used in a variety of analytical techniques including ICP.
Katanax Fusion Fluxers are the ideal fusion instruments for preparing difficult samples for ICP. Electric fusion fluxers are able to dissolve the most difficult matrices into a solution in minutes.
Safe- No need for concentrated acids or HF
Fast- Solid sample to solution in 20 minutes
Efficient- Difficult samples such as silica, alumina, zirconium and titanium can be dissolved
No metal contamination- Use of ceramic parts eliminates metal contamination
A full range of fusion fluxes are available for different sample types including non-borate fluxes. Crucibles are also available in platinum or graphite.

Symalab is specialized in the manufacture and distribution of technical consumables and equipment for AAS, ICP and ICP-MS. Distributor since 2013 of the company Precision Glassblowing, our range, made up of original manufacturer parts, covers the needs ranging from consumables for sample changers, nebulizers, torches, peristaltic pump tubes to cones for ICP-MS, spray chambers, connectors...
In 2018, we became a direct distributor of the Environemental Express brand, manufacturer of HotBlock® heating blocks and associated consumables (PP tubes, Filtermates, Flipmates, etc.).
That same year, we entered into a distribution partnership with GBC Scientifics to represent their ICP-TOF-MS model: truly simultaneous ICP-MS analysis.
Creator of the concept, we are the manufacturers of the PureProtec® removable protection enclosures with HEPA 13 ventilation and filtration. This allows you to protect your sample changers, heating blocks and especially your staff. Our advantage: we adapt to your constraints and not the other way around.
Equipped with a professional 3D printer FDM and SLA, our design office can produce your unique pieces or small series with ultra-trace quality plastics.
We are also one of the few specialists in consumables for CHONS (Dumas) - protein analysis by combustion where we distribute/manufacture tin, silver, brass, reagents, quartz or metal tubes, etc.
Finally, our company is an official distributor of the Altec brand, manufacturer of the AMA 254 mercury analyzer without sample preparation.

Thermo Fisher Scientific Inc. is the world leader in serving science, with revenues of more than $20 billion and approximately 70,000 employees globally. Our mission is to enable our customers to make the world healthier, cleaner and safer. We help our customers accelerate life sciences research, solve complex analytical challenges, improve patient diagnostics, deliver medicines to market and increase laboratory productivity. Through our premier brands – Thermo Scientific, Applied Biosystems, Invitrogen, Fisher Scientific and Unity Lab Services – we offer an unmatched combination of innovative technologies, purchasing convenience and comprehensive services.

We are proud to be supporting the 2019 European Winter Conference on Plasma Spectrochemistry and look forward to meeting you at our booth to show you powerful, easy-to-use solutions for routine and research trace elemental analysis.

Thermo Scientific trace elemental analysis instruments deliver quality, reproducible data from any sample type. With a streamlined and intuitive interface, our innovative solutions make it easy for operators at any experience level to analyze samples in accordance with even the strictest regulations and legislation, so you can have total confidence in your results.

Learn more at thermofisher.com/TEA

TOFWERK designs and delivers state-of-the-art time-of-flight (TOF) mass spectrometers (MS) for a broad range of laboratory and field applications. Our research product line includes the icpTOF, Vocus PTR-TOF, IMS-TOF, and EI-TOF for GC. Additionally, our engineers and scientists collaborate with research laboratories and OEM customers to develop custom MS solutions based on our modular design platform.

At the 2019 European Winter Conference on Plasma Spectrochemistry, we are spotlighting our icpTOF, which couples the Thermo Scientific iCAP RQ to a TOFWERK TOF mass analyzer. The iCAP QR provides versatile sample introduction, robust ICP, simple access to cones and lenses and the Qcell technology. The TOF adds simultaneous all-element detection, linear response and mass resolving power >6000, while maintaining QMS-equivalent sensitivity. With high-speed mass spectral acquisition and simultaneous analysis of all isotopes, the icpTOF is the ideal ICP-MS detector for multi-element single particle analysis or laser ablation imaging.

More information at: https://www.tofwerk.com/products/icptof/

TELEDYNE CETAC TECHNOLOGIES. Teledyne CETAC Technologies is a worldwide leader in sample introduction and sample handling equipment for elemental analysis. For over 25 years CETAC has been supplying high quality products that help atomic spectrometrists do more with their atomic absorption, inductively coupled plasma atomic emission and inductively coupled plasma mass spectrometry equipment, expanding the scope of possible measurements and pushing the boundaries of productivity. CETAC products and services are used in every industry where rapid and accurate determination of elemental trace levels are required, including semiconductor manufacturing, environmental analysis and petrochemical manufacturing. Headquartered in Omaha, Nebraska, USA, CETAC also maintains a European office in the UK, and is connected to a global network of distributors and service providers. www.teledynecetac.com

Triskem International SAS. Founded in 2007, Triskem International SAS is an independent French company that develops, manufactures and commercialises highly selective resins used in the separation, purification and recuperation of specific elements. Triskem Resins are used for

- Environmental monitoring, decommissioning and radiation protection
- Matrix removal and high precision determination of isotope ratios (dating/geochronology/nuclear forensics/food provenancing)
- Production and quality control of radio metals for medical use and recuperation of target materials
- Removal of pollutants before effluent release

TrisKem's expertise in separation chemistry and its wide range of resins with different selectivities provides a number of opportunities to solve analytical problems through sample preparation.
Frequently the problems encountered are centred on removing matrix interfering with the instrumental measurement.
ICP-MS is an example. Isobaric interferences have often to be removed in order to allow accurate determination of your analytes.
Selectivity for the analyte of interest is important in these cases. Extraction chromatography is widely used in various analytical applications, food provenancing, in geochronology and dating (e.g. U/Pb, Nd/Sm, Sr isotope ratios,...).
Since 2009, Triskem International has set up Research and Development projects in collaboration with universities and research centres worldwide.
Our R&D team is working on the development of new resins and methods in order to help you with your separation needs. Having a special separation need, willing to participate in a R&D project or looking for a partner to commercialize a new technology you have developed, please do not hesitate to contact us.
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Website: www.triskem.com - Contact: Steffen Happel - shappel@triskem.fr

UT2A Training & Consulting is born from researchers' willing to share their know-how in the domains of inorganic analysis and speciation. Trainings & consulting UT2A is a training centre, spin-off of the University of Pau and the Adour Countries (UPPA), and partner of the Bio-inorganic Analytical Chemistry laboratory and Environment / IPREM (UMR CNRS / UPPA 5254). Hardly with more than 18 years of experiment in the organization of training courses, and accompanied by more and more numerous experts in other analytical sciences than those who constitute our heart of business, we are at your disposal to help you develop the field of your analytical activities.
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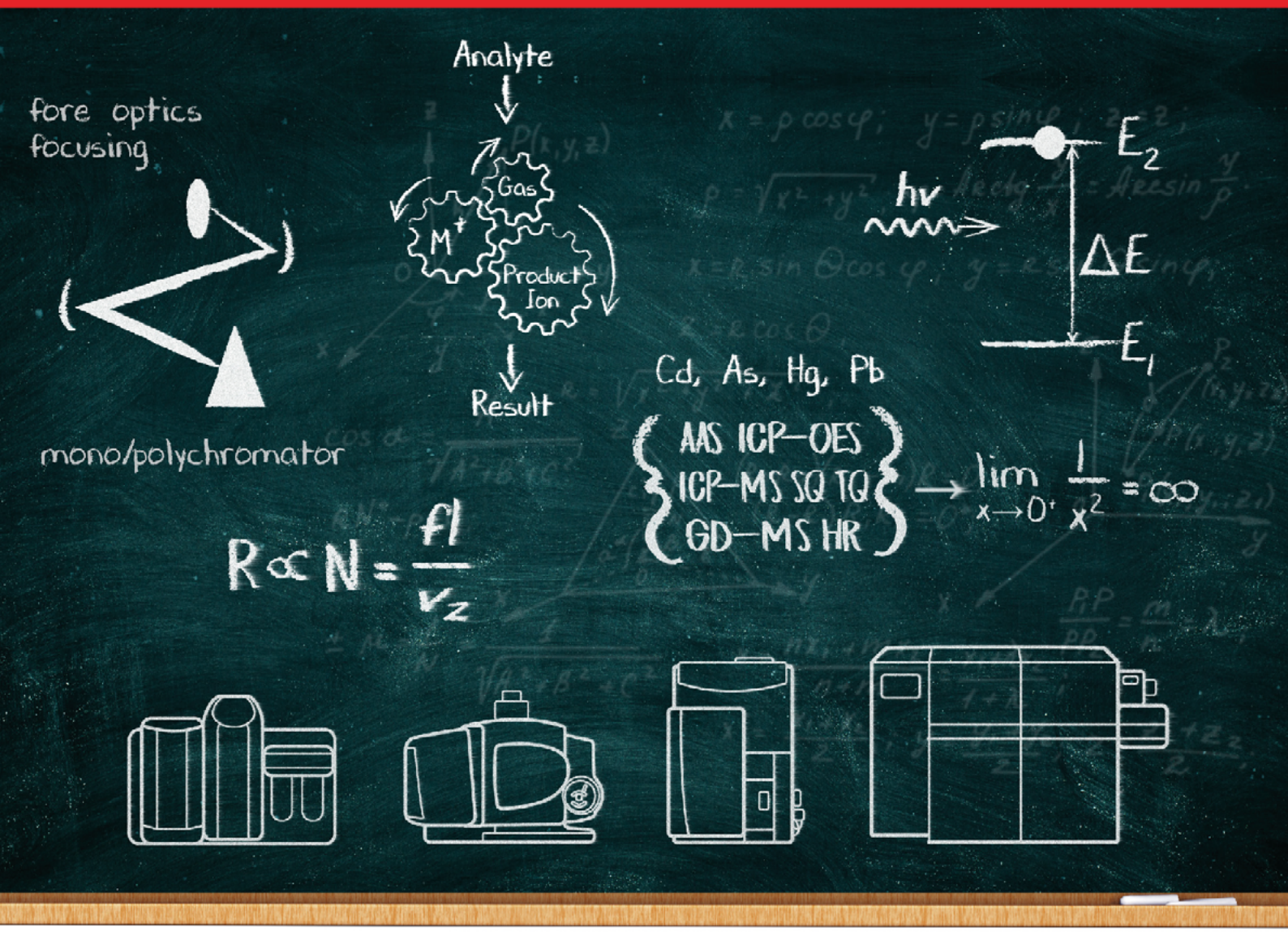

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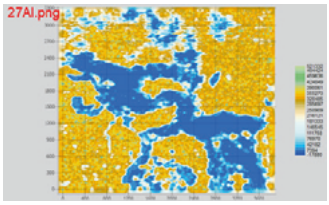

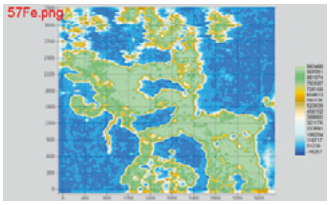

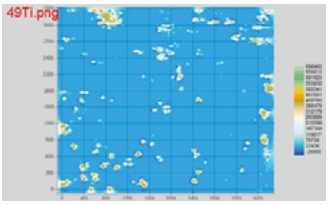

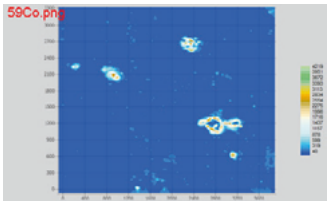

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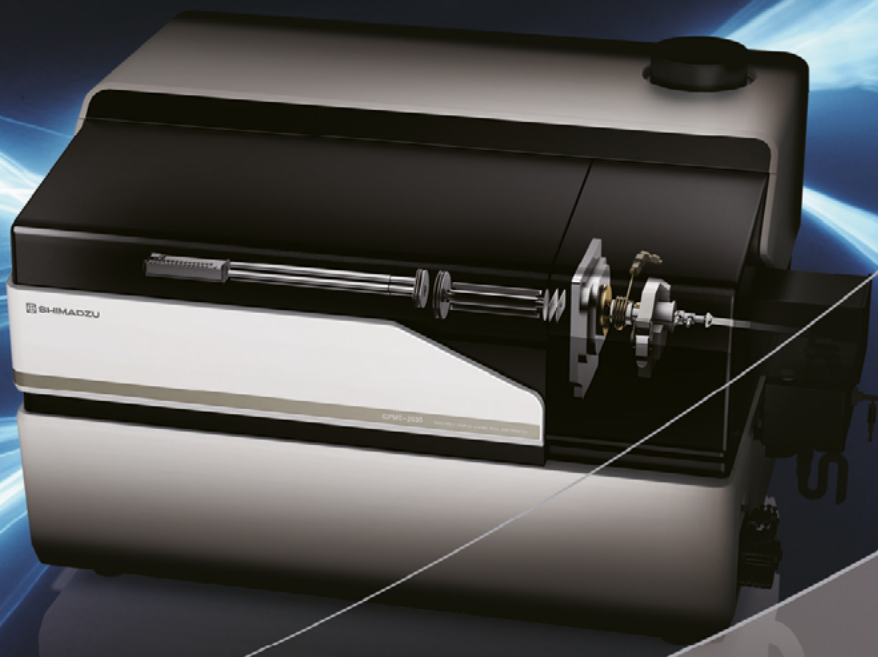

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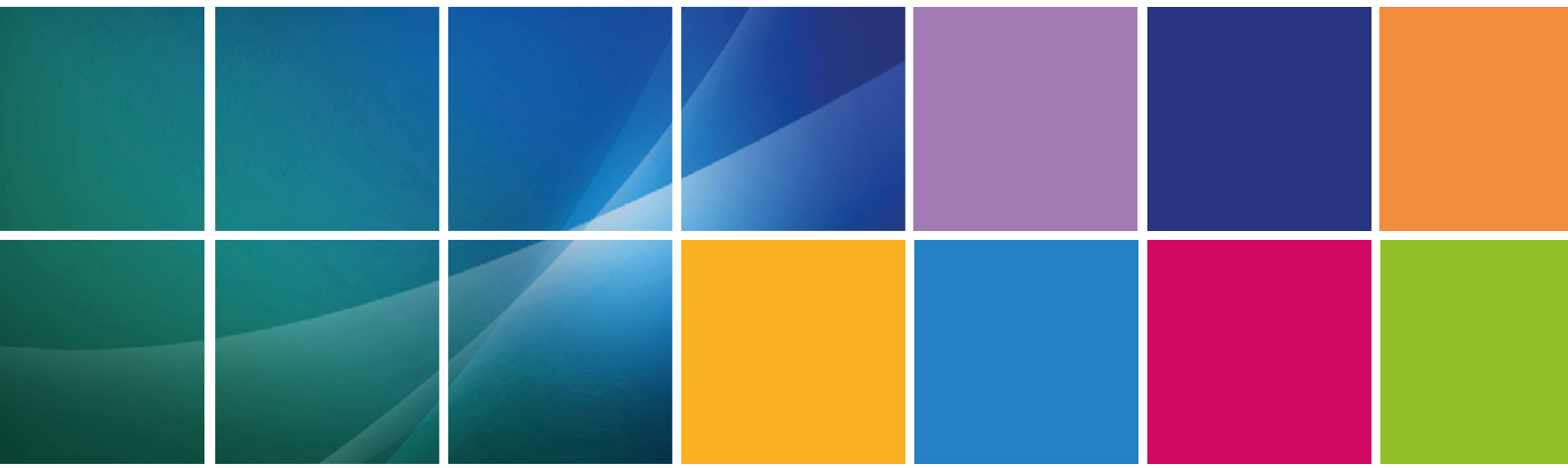

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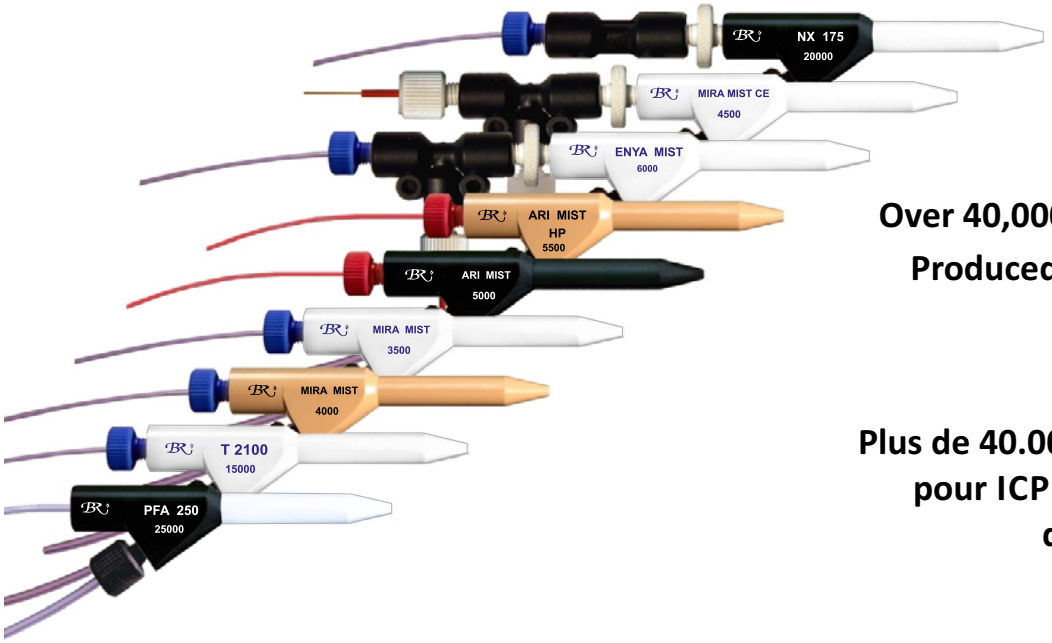

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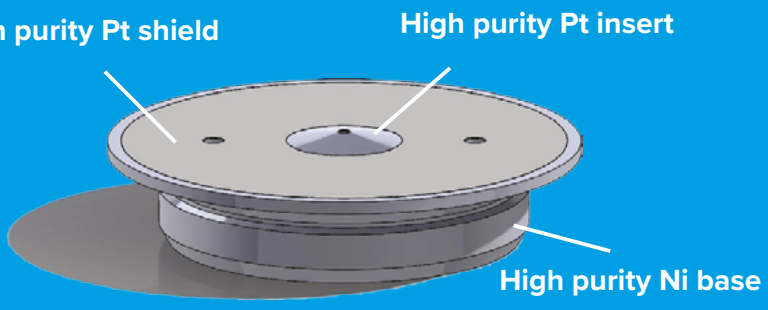
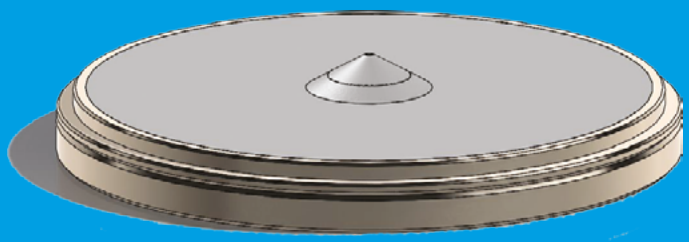


SC4014ps-Pt: compare to (N8145028)

VG1026ps-Pt: compare to (3601289)



HP2006ps-Pt: compare to (G3280-67056)

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CETAC products and services are used in every industry where rapid and accurate determination of elemental trace levels are required, including semiconductor manufacturing, environmental analysis and petrochemical manufacturing. Headquartered in Omaha, Nebraska, USA, CETAC also maintains a European office in the UK, and is connected to a global network of distributors and service providers.

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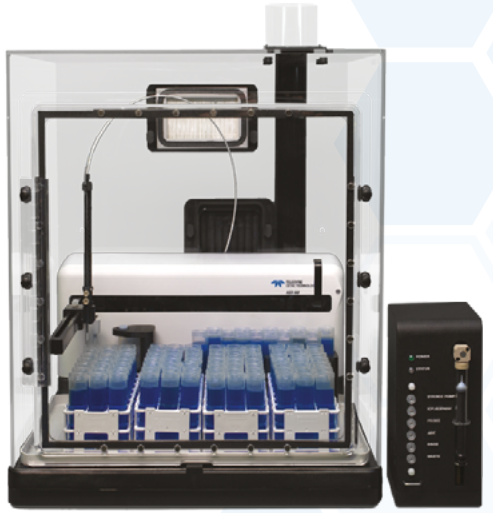
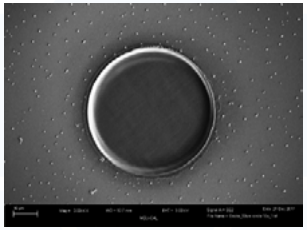
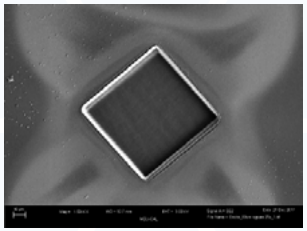


SDX HPLD

SimPrep

Aridus3





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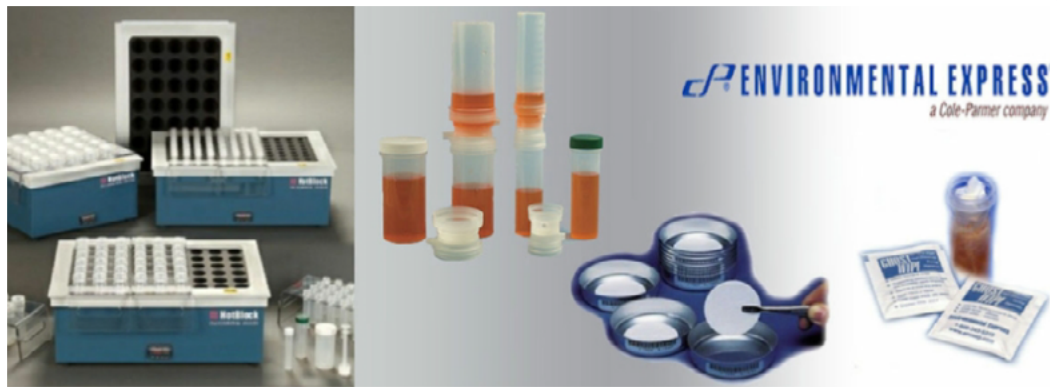

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2020 Winter Conference on
Plasma Spectrochemistry
Tucson, Arizona, January 12 – 18, 2020

The **2020 Winter Conference on Plasma Spectrochemistry**, 21st in a series of biennial meetings sponsored by the *ICP Information Newsletter*, features developments in plasma spectrochemical analysis by inductively coupled plasma (ICP), dc plasma (DCP), microwave plasma (MIP), glow discharge (GDL, HCL), and laser sources (LA, LIBS). The meeting will be held Monday, January 13 through Saturday, January 18, 2020, in Tucson, Arizona, (www.visitTucson.org) at the El Conqistador Tucson Resort (www.hiltonelconquistador.com). Professional development short courses at introductory and advanced levels and manufacturers' seminars will be offered Friday through Monday, January 10-13. Spectroscopic instrumentation and accessories will be shown during a three-day exhibition from January 14 to 16, and workshops on New Plasma Instrumentation, Clinical ICP-MS, Isotope Analysis, Elemental Imaging and Mass Cytometry, and Elemental Speciation methodology will be presented Tuesday thru Friday afternoons.

The continued growth in popularity of plasma sources for atomization and excitation in atomic spectroscopy and ionization in mass spectrometry and the need to discuss recent developments of these discharges in spectrochemical analysis stimulated the organization of this meeting. The Conference will bring together international scientists experienced in applications, instrumentation, and theory in an informal setting to examine recent progress in the field. Approximately 500 participants from 30 countries are expected to attend. Over 300 papers describing applications, fundamentals, and instrumental developments with plasma sources will be presented. The title submission deadline is July 12, 2019.

Six plenary and 34 invited lectures will highlight advances in these areas. Four afternoon poster sessions will feature applications, automation, and new instrumentation. Six Heritage Lectures will be presented by distinguished scientists and investigators, who have contributed significantly to the development of plasma spectrochemistry and will address critical development areas in sample introduction, instrumentation, elemental speciation, plasma source mass spectrometry, and novel software and hardware. Awards for outstanding young investigators and senior researchers also will be presented. Plenary, invited, and submitted papers will be published in September 2020 as the official Conference proceedings.

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Agilent activities at EWCPS 2019

Agilent continues to give the strongest support to the Atomic Spectroscopy community, contributing to new solution developments and supporting the "European Plasma and Rising Star" awards.

Don't miss the chance to win the "elemental travel mug" by playing our virtual game at the Agilent booth.

Software Demo

Monday to Friday
Agilent booth

ICP-MS MassHunter and ICP GO live demos.

03 ICP-MS/MS fundamentals

Sunday 03 February
13:30 - 16:30

Understanding Mechanisms of ICP-MS/MS for Resolving Polyatomic, Isobaric, and Other Spectral Interferences.

04 MassHunter Workshop

Monday 04 February
17:30 - 18:30
Auditorium Alphonse de Lamartine

Hands on workshop on MassHunter Software for ICP-MS and ICP-QQQ.

05 Lunch Seminar

Tuesday 05 February
12:25 - 14:00
Room Alphand

Pushing boundaries in Life Science Research.

Lunch box will be offered.

06 Company Night

Wednesday 06 February

Join us for a fun evening with delicious food at the Hippodrome. Availability is limited so please book your place early to avoid disappointment.

Register here: www.agilent.com/en/promotions/agilent-at-ewcps2019